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AMEN HOUSE, LONDON, E.C.4

CHANGES IN LEAF LITTER WHEN PLACED ON THE SURFACE OF SOILS WITH CONTRASTING HUMUS TYPES

I. LOSSES IN DRY WEIGHT OF OAK AND ASH LEAF LITTER*

K. L. BOCOCK, O. GILBERT,[1] C. K. CAPSTICK,[1] D. C. TWINN,[2] J. S. WAID,[3] AND M. J. WOODMAN

(The Nature Conservancy, Merlewood Research Station, Grange-over-Sands, Lancashire)

Summary

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Experimental Sites

The experimental areas in Roudsea Wood were situated in mixed coppice woodland growing on two parallel ridges, one of Carboniferous limestone and the other of Silurian slate. Although the soils on both sites may be classified broadly as brown forest soils the soil overlying slate is much more acid than that overlying limestone. Determinations made *in situ* in the top 5 cm. of the mineral soil, using a glass electrode placed in the moistened soil, indicated a reaction of pH 5·6–6·3 on the limestone and pH 3·2–4·7 on the slate site. These values correspond

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very closely to those obtained by Gorham (1953) for Lake District brown forest soils with mull and mor humus formations respectively. The humus forms of the soils on our sites have been designated mull on the limestone and moder on the slate. The diagnosis of the moder is based on the following characteristics as given by Kubiena (1953): the presence of a pronounced humus layer, very acid in reaction and containing much comminuted browned plant remains which are mixed together and not matted as in raw humus; loose bleached mineral grains permeate this mixture and the droppings of small soil animals are common. The L, F, and H layers are approximately of equal thickness.

The soil profiles, as they appeared in June, 1959, are described below.

Mull Site

Parent material probably glacial drift of Silurian shaly flags and grits with some Carboniferous limestone residue admixture. Drainage free to excessive.

L + F	3–0 cm.	Small twigs, stems, and some semi-skeletonized litter.
A	0–5 cm.	Dark brown[1] (7·5 YR 4/4) silty loam, occasional small stones of shaly flags and limestone; just moist; strong crumb and weak cloddy structure; porous; friable; moderate to high organic matter; abundant roots; merging into
(B)	5–25 cm.	brown (7·5 YR 3/2) silty loam to loam, stony as above; moist; moderate strong crumb; porous; friable; moderate organic matter; abundant roots; variable depth averaging 25 cm. over Carboniferous limestone, CD horizon.

Moder Site

Parent material, glacial drift derived from Silurian flags, shales, and grits overlying Bannisdale slates. Drainage free.

L	3–0 cm.	Small twigs, oak leaf litter, some birch and hazel litter.
A_1	0–4 cm.	(F 1·5 cm., H 2·5 cm.). Black (10 YR 2/1) organic loam with frequent small angular shale flag stones; moist; strong small cloddy structure in H layer; porous; friable; very high organic matter; abundant roots; fairly sharp boundary to
A	4–10 cm.	dark yellowish-brown (10 YR 3/4) silty loam, stony as above; moist; moderate medium to large crumb structure; porous; friable; high organic matter; abundant roots; fairly sharp boundary to
(B)	10–45 cm.	strong brown (7·5 YR 5/6) gritty silty loam with abundant small and medium, occasional large, stones of flags and fine sandstones; moist; moderate medium crumb structure; porous; friable to slightly sticky; frequent tree roots; fairly sharp boundary to
C	45–65 cm.	pale olive (5 Y 6/3) with increasing yellowish red mottle below; gritty silty clay loam, stony as above; very weak medium to large crumb; moderately porous; massive and hard initially, sticky when wet; occasional roots in upper part.

[1] Munsell soil-colour names used in descriptions.

The areas carried coppice with standards from about 1844, but many of the standard oak trees were felled during the two world wars and the remainder in 1946. From 1844 to 1904 the coppice was cut on a 15-year rotation but since that date the coppice falls have been more irregular. The coppice canopy on the present mull site is about 6 m. high whilst on the moder site it is about 9 m. high. Details of the composition of plant communities on the two sites are given in Table 1.

Six rain-gauges were placed in each experimental area and the amount of precipitation measured at weekly intervals. Air temperature at each site was measured with an unscreened maximum and minimum thermometer placed 30 cm. above the soil surface. Rainfall data have been included

TABLE 1

The Composition of the Plant Communities on the Two Experimental Sites, each with 24 Plots, Summer, 1957

Layer	*Species*	*% cover*	
		Limestone site with mull humus form	*Slate site with moder humus form*
(i) *Coppice shrubs* Mean % canopy cover/plot provided by each species with no allowance for overlapping of canopy layers	*Corylus avellana*	65	10
	Fraxinus excelsior	23	0
	Betula verrucosa	19	19
	Crataegus monogyna	3	0
	Quercus petraea	0	71
(ii) *Herbs* Mean % ground cover/plot		65	50
(iii) *Bryophytes* Mean % ground cover/plot		39	0
	The more abundant species in the herb layer	*Number of plots in which the species was present*	
		Mull	*Moder*
	Rubus agg. sp.	24	0
	Viola spp.	24	0
	Stachys sylvatica	22	0
	Convallaria majalis	21	0
	Mercurialis perennis	19	0
	Brachypodium sylvaticum	19	0
	Anemone nemorosa	19	0
	Ajuga reptans	14	0
	Deschampsia flexuosa	0	24
	Pteridium aquilinum	0	21
	Lonicera periclymneum	0	20
	Oxalis acetosella	0	10

in Fig. 4 and these, together with the temperature readings, show that there was no appreciable macro-climatic difference between the two sites during the period of study. As the sites were only 500 m. apart and at a similar altitude, this was to be expected.

Materials and Methods

The ash and oak leaves were collected from two groups of trees growing on limestone near the Merlewood Research Station. To prevent contamination from the soil the leaves were collected during leaf-fall in

nets suspended beneath the trees; these nets were emptied daily and the leaves air-dried in an unheated and well-ventilated room where they were stored for a few days until required. Sub-samples of this material were weighed in 1-cm.-mesh hair-nets which were closed by tying the elastic. Each net contained twenty ash leaflets or eight oak leaves weighing approximately 2 g.

The nets containing oak and ash litter were placed on the surface of the soil at the two sites on 14 and 16 November 1956, respectively. On each site the twenty-four plots, each measuring 150 by 120 cm., were arranged as compactly as possible in pairs. In one randomly selected member of each pair were placed twelve nets of oak leaves and in the other, twelve nets of ash leaflets. Each net was anchored in position by means of an anodized aluminium label and was not less than 30 cm. from its nearest neighbour. The contents of randomly selected nets, twelve nets per species, were oven-dried to constant weight at 105° C. in order to obtain the mean initial moisture contents of the air-dry experimental material. These values, oak 13·6 per cent. (S.E. 0·4), ash 16·1 per cent. (S.E. 0·7), were used to calculate the initial oven-dry weights of all samples placed in the field. Sampling was carried out periodically, ash being sampled more frequently than oak. On each sampling occasion one net was selected at random from each plot and placed in a polythene bag for transportation to the laboratory. The contents of each net were sorted separately, the leaves counted, and visible animals and extraneous mineral matter removed. The estimate of the number of leaves remaining in a net was based on the number of recognizable midribs present. The dry weight of each sample was then determined after drying at 105° C.

The cold-water-soluble material present initially in the oak or ash litter was determined using three to four accurately weighed replicates, each consisting of about 0·5 g. air-dry powder or whole oak leaves or ash leaflets. Each sample was placed in a conical flask with 25 ml. thymol-saturated distilled water and wetted under reduced pressure in a vacuum desiccator. The flasks were then stoppered and allowed to stand for three days at room temperature with occasional agitation on a Microid shaker. After a final shaking of 2 hours the contents of each flask were filtered on a tared filter-paper and the residual litter washed until the filtrate was colourless. The dry weight of each residue was determined by drying at 105° C. to constant weight.

As a measure of the possible effects of the respiratory activity of the litter micro-organisms during the initial period of the loss in dry weight, 0·5-g. samples of the litter were shaken with 25 ml. distilled water in 250 ml. conical flasks for a week at room temperature and the loss in weight determined by oven-drying.

Results and Discussion

The oak leaves on both sites disappeared very slowly from the nets (Fig. 1); ash litter disappeared more quickly, but showed a marked difference between the two sites. On the mull, ash disappeared so rapidly that, after about 6 months, only a few leaflet mid-ribs remained

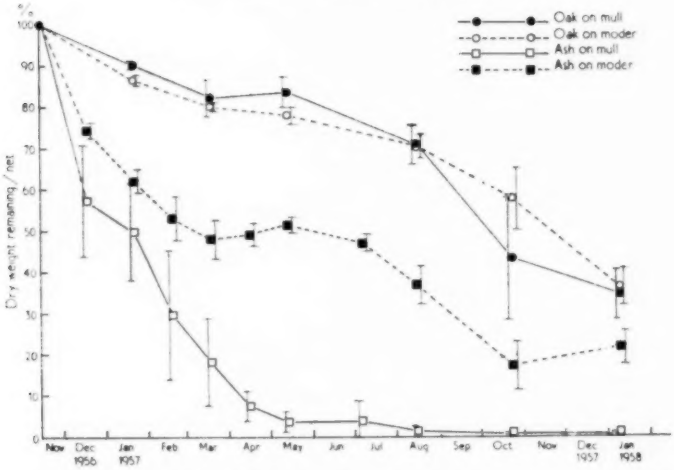

FIG. 1. Percentage of the original dry weight remaining on a per net basis. Means ± 95 per cent. confidence limits.

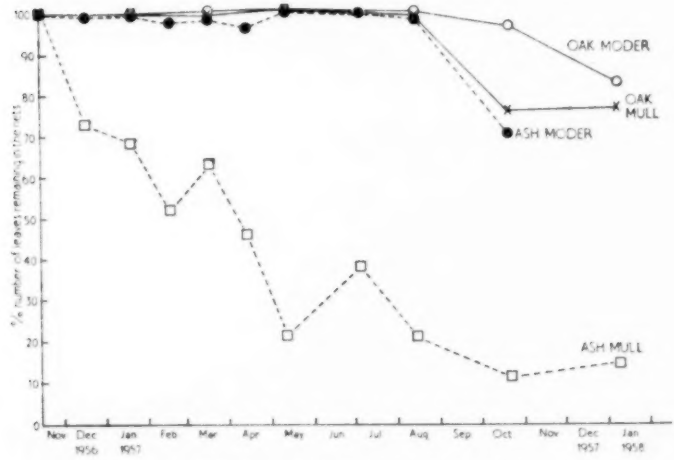

FIG. 2. The loss of whole leaves from the nets.

in the nets; not only was there loss of material from the nets by skeletonization, but also loss of whole leaflets (Fig. 2). In contrast, disappearance of ash litter on the moder was slow and followed a different course, few if any whole leaves being removed. On the mull site oak leaves may be pulled out of the nets by earthworms less easily than the more flexible ash leaflets. However, this effect is unlikely to affect the results significantly, in the first few months of decomposition, because

earthworms tend to select nitrogen-rich litter such as ash in preference to oak litter if both are available (Wittich, 1953). We noticed that the deep-burrowing earthworms living beneath oak trees on the mull fed mainly on ash, hazel, and birch litter during the 6 to 8 months following leaf-fall. After this period both the natural oak litter and the experimental material were attacked by earthworms.

In order to obtain an estimate of the losses taking place from the leaves remaining inside the nets, as distinct from the losses due to the removal of whole leaves, we have also calculated our results on a per

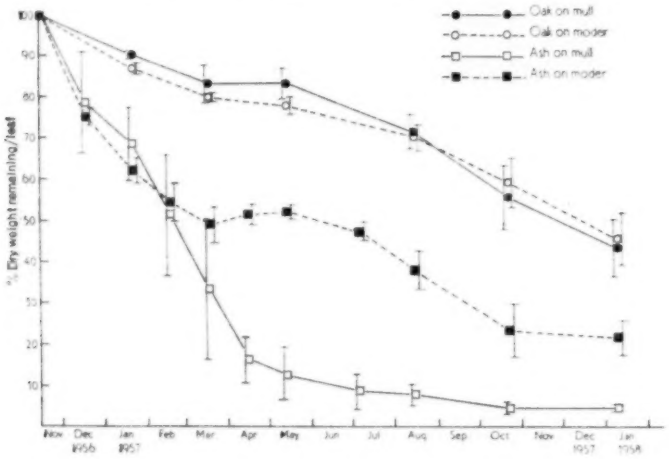

FIG. 3. Percentage of the original dry weight remaining on a per leaf basis. Means ± 95 per cent. confidence limits.

leaf basis (Fig. 3), the final mean weight per leaf being expressed as a percentage of the initial mean weight per leaf. On this basis, the results obtained show, as expected, little difference in the rate of disappearance of oak-leaf material on the two sites. Similarly, ash litter disappeared at about the same rate on both sites during the first 3 months; thereafter, there was a striking difference between them.

The rates of loss of dry matter per leaf per day for the leaves remaining in the nets are given in Fig. 4. The high rates of dry-matter loss during the first few weeks can be explained largely by the decrease in the water-soluble component. Previous workers have shown that the freshly fallen leaves of very many trees contain large amounts of water-soluble materials (Lossaint, 1956; Melin, 1930; Mikola, 1954; Saitô, 1957; Viro, 1955; Wittich, 1943). We have shown in field experiments using ash and oak litter that the hot-water-soluble fraction decreases markedly during the first few weeks of decomposition (Gilbert and Bocock, 1960); in oak litter, however, the soluble fraction disappeared more slowly than it did in ash litter—which can be explained in terms of the accessibility of the soluble material to water and microbial activity (Table 2).

Saitô (1957) has suggested that a similar decrease in cold-water-soluble material in beech litter is due to the leaching of this fraction by rain-water and its metabolism by micro-organisms. In this connexion, Waksman and Tenney (1928) stressed the nutritional importance to

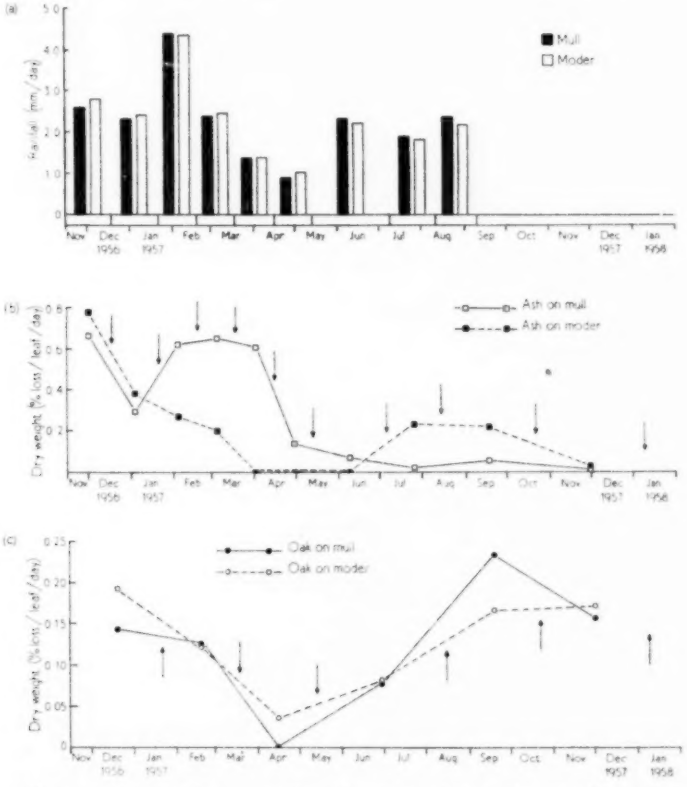

FIG. 4. (*a*) Rainfall, mean values for the periods indicated. (*b*) Rate of loss of dry matter per leaflet per day from ash leaflets remaining in the nets. (*c*) Rate of loss of dry matter per leaf per day from oak leaves remaining in the nets.

In (*b*) and (*c*) the vertical arrows indicate the positions of the sampling dates and the rate of loss of dry matter for a period between dates is indicated by a point midway between the two appropriate arrows.

micro-organisms of the water-soluble fraction of litter and amongst other investigators both Melin and Viro demonstrated that microbial decomposition is already proceeding in senescent leaves at leaf-fall. The results in Table 2 show that an appreciable loss in weight can occur very quickly in freshly-fallen damp litter as a result of microbial activity.

During late April and early May 1957 the rates of disappearance of both ash and oak litter were very low on both sites. This was a period of low rainfall and it is probable that the lack of moisture in the litter was then the overriding factor. However, during March and early April 1957 the rate of disappearance of ash on moder was low while on the mull site it reached its peak; at this time the litter was relatively dry on both sites.

TABLE 2

Loss in Dry Weight of Litter at Room Temperature in the Laboratory Experiments

	% loss of cold-water-soluble material after 3 days' extraction						*% respiratory loss in cold water after 7 days*					
	whole leaves			*leaf powder*			*whole leaves*			*leaf powder*		
	$\bar{X}$	S.E.	*n.*	$\bar{X}$	S.E.	*n.*	$\bar{X}$	S.E.	*n.*	$\bar{X}$	S.E.	*n.*
Ash	20·79	0·49	4	23·14	0·99	3	5·18	0·29	3	5·71	0·48	4
Oak	10·33	0·46	4	18·52	0·79	4	3·77	0·24	3	3·88	0·41	4

TABLE 3

Coefficient of Variation of the Standard Deviation of Percentage Loss in Dry Weight of Oak and Ash Litter on a Per Leaf Basis

	1956	*1957*								*1958*
	Dec.	*Jan.*	*Feb.*	*Mar.*	*Apr.*	*May*	*July*	*Aug.*	*Oct.*	*Jan.*
Oak–Moder	..	15·1	..	7·5	..	14·0	..	14·9	22·0	18·2
Oak–Mull	..	15·0	..	41·2	..	34·7	..	23·2	24·4	19·7
Ash–Moder	11·8	12·4	14·4	12·5	7·3	5·0	6·0	12·7	13·8	8·4•
Ash–Mull	86·8	39·5	42·8	38·7	9·9	12·0	7·0	4·2	2·3	3·1

• Estimate based on per net results.

It is suggested that temporary drought had far less effect on the mull than on the moder site. On the moder the organisms responsible for the decomposition and disappearance live in the surface layers; when the litter dries out their activities there cease temporarily. On the mull, on the other hand, much of the disappearance of organic matter is believed to be due to relatively large invertebrates, especially the earthworm *Lumbricus terrestris* L. This species occupies the mineral soil during the day and is active in the litter during the night drawing material into the mouth of its burrow. Only after a prolonged shortage of rain are its activities curtailed. That different agents are responsible for ash litter disappearance on the two sites is evidenced by the results shown in Fig. 2. It is obvious that powerful mechanical forces, probably earthworms, are at work on the mull. Differences between the sites are corroborated by comparisons of the coefficients of variation (Table 3).

It is arguable that experiments using nylon hair-nets merely demonstrate the effect of these nets on litter break-down. However, whilst experiments using this technique are somewhat artificial, they have

yielded results which clearly differentiate the two sites. The mechanisms underlying the differences can as yet be only guessed and their elucidation requires further study.

Acknowledgements

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CHANGES IN LEAF LITTER WHEN PLACED ON THE SURFACE OF SOILS WITH CONTRASTING HUMUS TYPES

II. CHANGES IN THE NITROGEN CONTENT OF OAK AND ASH LEAF LITTER[1]

O. GILBERT[2] AND K. L. BOCOCK

(*The Nature Conservancy, Merlewood Research Station, Grange-over-Sands, Lancashire*)

Summary

Different trends have been demonstrated in the changes in composition taking place in sub-samples of the same ash litter placed in nylon hair-nets on neighbouring sites with mull and moder-type humus forms. Similar trends have been shown to occur for oak litter and ash litter placed on the same moder site. The percentage nitrogen content of ash litter on the mull site remains virtually constant during the first 7 months of decomposition whereas on the moder site the content increases steadily for both ash litter and oak litter. The nitrogen content of oak litter is increased by considerable addition from outside. Possible sources of this additional nitrogen are considered. Extraction with hot water of litter at different stages of decomposition shows that the initially large water-soluble fraction, which is poor in nitrogen, is leached out more quickly from ash than from oak litter.

Introduction

DIFFERING rates of dry-weight loss of various litters placed on soils with contrasting humus types have been reported in previous papers (Bocock and Gilbert, 1957; Bocock *et al.*, 1960). In this paper the results are given of studies, made possible by the use of the nylon hair-net technique already described (Bocock and Gilbert, 1957), of the changes in composition occurring in leaf litter lying on the soil surface. Previous workers have stressed that differences in the metabolism of nitrogen in the two types of humus formation, mull and mor, are of fundamental significance (Romell, 1935; Handley, 1954) and this aspect has received our special attention. The experiments described in this paper form part of a study of the roles played by heterotrophic organisms in the breakdown of litter.

Materials and Methods

(*a*) *Preliminary treatment of samples*

The ash and oak leaves used in these experiments were sub-samples of the material used for the study of dry-weight losses (Bocock *et al.*, 1960). Approximately 3 g. of air-dry leaves, i.e. 30 ash leaflets or 14 oak leaves, were placed in each net which was then closed by tying the elastic. The samples for chemical analysis were placed within the same experimental areas as the dry-weight samples (Bocock *et al.*, 1960) and similarly were anchored to the ground with anodized

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labels. In contrast to them, however, two nets were attached to each label and arranged to the right and left of the rows of labels, each net being at least 20 cm. from any adjacent net. On the moder site, rows of five pairs of oak samples alternated with rows of a similar number of ash samples. Only ash samples were placed on the mull site but a few oak samples taken from the dry-weight experimental blocks were used for chemical analysis. The nets were placed in the field on 22 November 1956 and a sufficient number to provide at least 6 g. of air-dry milled material were taken up at each sampling date; the nets were selected at random. In the laboratory material was removed from a net by untying the knot in the elastic, thus avoiding any contamination of the samples with nylon threads. All visible invertebrates and mineral matter were removed and the leaves in each net counted.

After sorting, the bulked samples were dried to crispness in a 1-litre wide-mouthed flask at 35°–40° C. under reduced pressure on a rotary film evaporator (Craig *et al.*, 1950; Bocock and Gilbert, 1956). No appreciable change in total nitrogen, as a percentage of oven-dry weight, occurred during the drying and it is believed that the anaerobic conditions caused by the reduced pressure inhibited microbial action (Gilbert and Bocock, 1958). The dried leaves were milled in a Casella grain mill to a particle size of less than 0·5 mm., care being taken to avoid overheating of the samples by grinding too rapidly. Milled samples were stored in polythene-stoppered tubes at below −8° C. until required for analysis.

(*b*) *Analytical techniques*

The milled material was used for all chemical analyses and in order to place all the results on an oven-dry weight basis the moisture content of the sample was determined in each case by drying three 50-mg. subsamples to constant weight at 105° C.; the percentage combustible matter was determined by heating these samples in a muffle furnace at 650° C. for 3 hours. Total nitrogen content of four 50-mg. replicates of crude or hot-water-extracted material was determined using the following Kjeldahl technique. The mixture recommended by McKenzie and Wallace (1954), which effects rapid digestion at a high temperature, was used, additional sulphuric acid being added to offset that lost in oxidation of the plant material (Self, 1912). Each digestion took about 1–1½ hours, longer times of digestion for material rich in lysine and histidine (Chibnall, Rees, and Williams, 1943) being unnecessary as the maximal histidine and lysine contents as determined by paper chromatography were less than 1 and 3 per cent. respectively of the total nitrogen. Pyrex boiling tubes, 8 in. by 1 in., were used as digestion vessels (Beet, 1955). The distillation apparatus of Beet and Belcher (1938) was used with a silica condenser, a very even flow of steam being produced from a 5-litre flask with an immersion heater. The ammonia was collected in 2 per cent. boric acid and titrated with N/100 HCl. Blank determinations for the whole Kjeldahl procedure were carried out on each batch of reagents; the blank values for the distillation part of the procedure were checked before and after each series of distillations.

The carbon content of each litter sample was determined by the use of the wet combustion method of Van Slyke and Folch (1940). The carbon dioxide generated during the acid digestion was subsequently measured in the Van Slyke–Neill manometric apparatus.

To determine water-soluble material, 1 g. of powder was shaken for 30 min. in a 250-ml. thermos flask with 50 ml. of hot ammonia-free distilled water; after this time the water temperature had fallen from 75° C. to about 55° C. The powder was then washed out of the flask with about 150 ml. of ammonia-free water, filtered on a weighed filter paper and washed free of any gelatin-precipitating material. After the surplus water had drained away, the wet powder was dried on the filter paper in a vacuum desiccator, equilibrated with room air and reweighed. As a control, a tared filter paper was kept in the same room as the paper bearing the extracted powder and reweighed when the latter was reweighed. Sub-samples of the extracted powder were taken for moisture determinations and the extractable material calculated using the appropriate air-dry to oven-dry conversion factors. The pH of the undiluted water extract was determined using a glass electrode. As an indication of the protein-precipitating ability of the extract, 5 ml. was mixed with 1 ml. of 1 per cent. gelatin in 10 per cent. NaCl containing 0·15 per cent. methyl parahydroxybenzoate as a preservative. Cold-water extracts, made by soaking litter powder in thymol-saturated water (1:5, w/v) overnight at 1° C., were used for protein tests.

Results

The nitrogen content of the crude ash litter (Table 1, Fig. 1) shows little variation during the course of decomposition on the mull site except for a slight initial rise. In contrast, on the moder site where disappearance is slower, the ash leaflets show an increasing nitrogen content until October, after which a slight decrease is recorded. Oak litter, which contains initially less nitrogen than the ash, shows a similarly mounting percentage nitrogen content when on the moder site. The two samples of oak litter taken from the mull site show an increased nitrogen content although a less significant one. A similar series of patterns is revealed

TABLE 1

Crude Litter: Total Nitrogen and Combustible Matter (C.M.) as a Percentage of Oven-dry Matter. Means ±95 per cent. Confidence Limits

Sampling date	*Ash*				*Oak*			
	Mull		*Moder*		*Mull*		*Moder*	
	N	*C.M.*	*N*	*C.M.*	*N*	*C.M.*	*N*	*C.M.*
22.11.56	1·48 ± 0·02	99·0 ± 0·2	1·48 ± 0·02	99·0 ± 0·2	0·73 ± 0·03	95·9 ± 0·2	0·73 ± 0·02	95·9 ± 0·2
7.1.57	1·63 ± 0·01	94·1 ± 0·3	1·93 ± 0·01	95·8 ± 0·1	..	..	..	..
4.2.57	1·62 ± 0·02	96·3 ± 0·8	..	..	..	..	1·02 ± 0·01	96·8 ± 1·4
4.3.57	1·58 ± 0·01	94·5 ± 0·4	2·21 ± 0·07	96·6 ± 1·0	..	..	..	..
1.4.57	1·65 ± 0·02	94·2 ± 1·7	..	..	..	..	1·03 ± 0·01	95·3 ± 0·3
6.5.57	1·57 ± 0·03	95·8 ± 1·0	2·41 ± 0·02	97·2 ± 0·6	..	..	..	..
3.6.57	1·55 ± 0·04	92·9 ± 0·9	..	..	..	..	1·20 ± 0·01	96·1 ± 0·6
1.7.57	..	..	2·58 ± 0·01	97·1 ± 0·3	..	..	1·34 ± 0·01	95·7 ± 0·2
4.10.57	..	..	2·81 ± 0·01	96·8 ± 0·8	1·30 ± 0·02	92·2 ± 1·4	1·83 ± 0·02	93·9 ± 0·4
9.1.58	..	..	2·65 ± 0·01	94·8 ± 0·8	1·22 ± 0·02	89·6 ± 0·9	1·90 ± 0·03	93·7 ± 0·7

when the nitrogen contents are expressed as a percentage of combustible matter (Fig. 1), showing that the main trends are not attributable to mineral contamination.

In a parallel experiment on the same sites the progressive losses of dry-weight material in the two litters have been followed (Bocock *et al.*, 1960). Taking the nitrogen values shown in Table 1 in conjunction with these dry-weight results, we have calculated the absolute

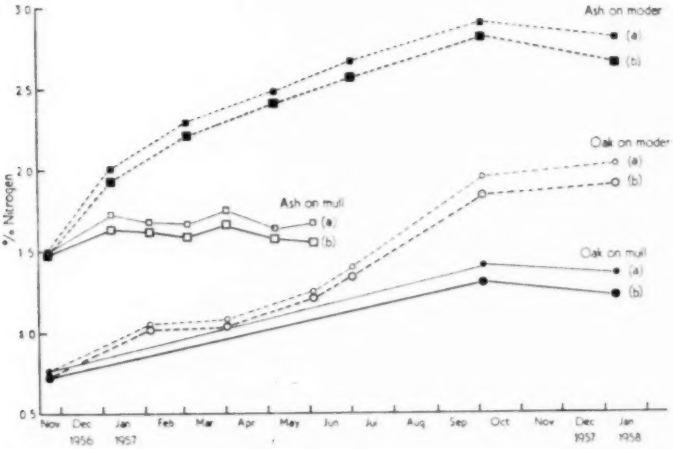

FIG. 1. Nitrogen content of crude litter, (*a*) as a percentage of combustible matter, (*b*) as a percentage of oven-dry matter.

amounts of nitrogen in the experimental samples at various dates. In Fig. 2 the absolute amounts of dry matter and nitrogen per leaf in the nets at various dates are shown as percentages of the amounts per leaf present in the nets initially. In ash on mull the percentage change in nitrogen is virtually identical with the dry-weight change, except for the initial divergence which is a reflection of the large amount of water-soluble material present initially but lost in the first month. In ash on moder an even wider divergence occurs during the first month. Thereafter the changes in nitrogen and dry weight are roughly parallel although this correspondence is not as close as that shown by ash on mull. The striking feature of oak litter, both on moder and on mull, is that, whereas the dry weight decreases slowly but steadily, the absolute amount of nitrogen in the samples increases over a period of 10 months and it is noteworthy that it does not decline until after the beginning of the next leaf-fall. Using the same data as above, and the carbon contents of the litter, the C/N ratios have been calculated both for the material remaining in the nets and, by difference, for the material lost from them. The ash litter remaining in the nets on mull has a fairly constant C/N ratio throughout decomposition (Table 2) and the C/N ratio of the material

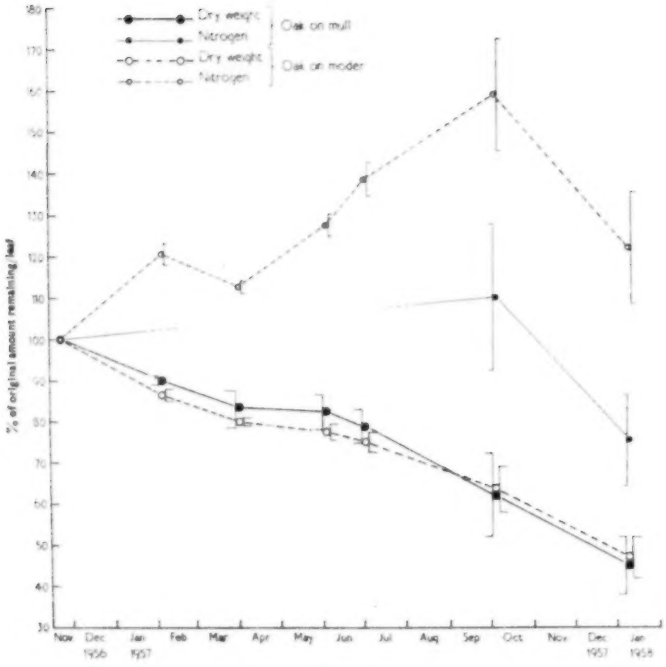

FIG. 2*a*

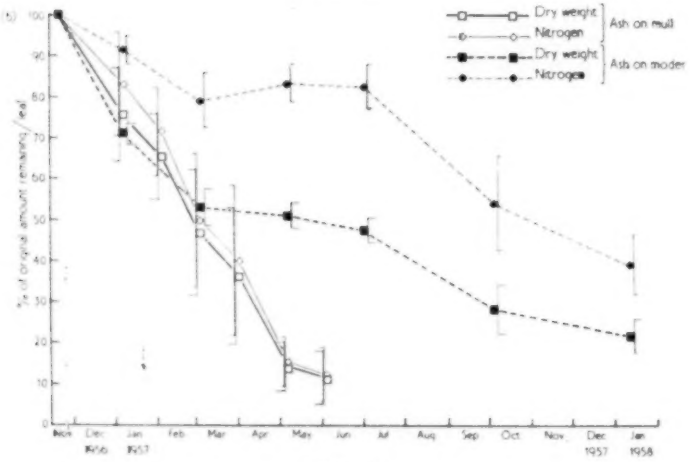

FIG. 2*b*

FIG. 2. Percentage of the original nitrogen and dry weight remaining in the nets. Means ± 95 per cent. confidence limits. The latter have been estimated for dry weight from the loss-in-dry-weight graph (Bocock *et al.*, 1960, Fig. 3) and for nitrogen from the dry-weight graph and mean per cent. nitrogen figures. (*a*) oak litter, (*b*) ash litter.

TABLE 2

Crude Litter: C/N Ratio of (a) Residual Litter in Nets, (b) Material Lost from Nets since Previous Sampling Date

Sampling date	Ash				Oak			
	Mull		Moder		Mull		Moder	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
22.11.56	35·2	..	35·2	..	71·9	..	71·9	..
7.1.57	31·7	52·4	26·3	146·4	..	..	..	..
4.2.57	32·5	26·5	..	..	..	..	47·9	N
4.3.57	33·7	29·7	24·0	39·5	..	..	..	..
1.4.57	31·2	44·3	..	..	..	..	47·7	50·0
6.5.57	33·3	30·3	22·0	N	..	..	..	..
3.6.57	30·8	42·0	..	..	..	..	43·4	N
1.7.57	..	..	20·2	220·0	..	..	35·5	N
4.10.57	..	..	18·2	24·3	35·5	N	28·5	N
9.1.58	..	..	18·7	16·8	37·2	31·5	26·2	35·9

N, N increase.

lost from the nets was shown to be similar to that for the residue in the nets except during the first 6 weeks. In contrast, ash litter on moder shows no similarity between material remaining and material lost except

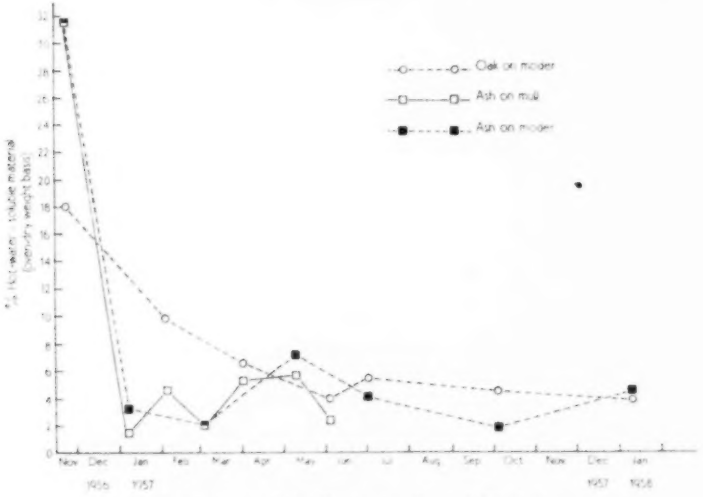

FIG. 3. Percentage of the litter powder soluble in hot water.

towards the end of the experiment; in fact, the residue shows a progressive increase in nitrogen content whereas the material lost is relatively poor in nitrogen. In oak litter on both sites, as in ash litter on moder, the C/N ratios of the material lost show little similarity to those

of the material remaining except possibly at the beginning of the second year of decomposition.

Hot-water extraction of milled material reveals that initially both oak and ash litters contain a large amount of readily soluble material, especially so in the case of freshly-fallen ash leaves (Fig. 3). The extracts were tested for their ability to precipitate gelatin (Table 3), a positive result being obtained only for oak litter extracts and in these only during the early stages of decomposition. In qualitative tests on the cold-water extracts of the time 0 samples using equal volumes of extract and reagent, 10 per cent. trichloracetic acid, a fairly specific protein precipitant (Hiller and Van Slyke, 1922; Hoch and Valler, 1953; Allport and Keyser, 1957) gave negative results. In general, the values for percentage nitrogen content and combustible matter of water-extracted powders show very similar trends to those for unextracted powders (Table 4). In November 1956, however, water extraction of the freshly-fallen ash litter caused a

TABLE 3

Crude Litter: Hot-Water Extract

Sampling date	*pH*				*Reaction with 1% gelatin solution*			
	Ash		*Oak*		*Ash*		*Oak*	
	Mull	*Moder*	*Mull*	*Moder*	*Mull*	*Moder*	*Mull*	*Moder*
22.11.56	5·6	5·6	4·9	4·9	—	—	+	+
7.1.57	6·4	5·7	..	..	—	—	..	..
4.2.27	6·2	..	..	4·6	—	..	..	+
4.3.57	5·9	5·8	..	..	—	—	..	..
1.4.57	5·6	..	..	4·5	—	..	..	—
6.5.57	5·9	5·5	..	..	—	—	..	..
3.6.57	5·8	..	..	4·4	—	..	..	—
1.7.57	..	5·5	..	4·9	..	—	..	—
4.10.57	..	5·4	5·2	5·5	..	—	—	—
9.1.58	..	5·4	5·9	5·1	..	—	—	—

\+ Strong ppt. — Negative result.

TABLE 4

Hot-water-extracted Litter: Total Nitrogen, Combustible Matter (C.M.) as a Percentage of Oven-dry Material. Means ±95 per cent. Confidence Limits

Sampling date	*Ash*				*Oak*			
	Mull		*Moder*		*Mull*		*Moder*	
	N	*C.M.*	*N*	*C.M.*	*N*	*C.M.*	*N*	*C.M.*
22.11.56	1·68 ± 0·02	95·4 ± 0·1	1·68 ± 0·02	95·4 ± 0·1	0·75 ± 0·06	96·2 ± 0·3	0·75 ± 0·06	96·2 ± 0·3
7.1.57	1·61 ± 0·02	95·3 ± 1·2	1·85 ± 0·05	95·9 ± 0·9	..	..	..	..
4.2.57	1·57 ± 0·03	95·6 ± 1·0	..	..	..	..	0·93 ± 0·02	96·2 ± 0·3
4.3.57	1·54 ± 0·05	95·8 ± 1·1	2·06 ± 0·01	97·0 ± 0·8	..	..	..	..
1.4.57	1·62 ± 0·04	95·6 ± 0·6	..	..	..	..	1·01 ± 0·01	96·3 ± ·08
6.5.57	1·51 ± 0·03	95·5 ± 2·5	2·40 ± 0·02	97·4 ± 0·3	..	..	..	..
3.6.57	1·42 ± 0·03	94·0 ± 1·5	..	..	..	..	1·18 ± 0·04	95·8 ± 2·1
1.7.57	..	..	2·61 ± 0·06	98·3 ± 0·6	..	..	1·40 ± 0·05	96·6 ± 0·4
4.10.57	..	..	2·69 ± 0·01	97·2 ± 0·4	1·30 ± 0·02	94·0 ± 0·5	1·80 ± 0·02	95·5 ± 2·2
9.1.58	..	..	2·76 ± 0·03	96·6 ± 0·3	1·46 ± 0·01	93·0 ± 1·5	1·96 ± 0·03	95·6 ± 3·0

considerable increase in the nitrogen content as a percentage of the oven-dry weight.

The pH values (Table 3) show that oak litter extracts tend to be more acid than ash litter extracts, and that mull extracts tend to give slightly higher pH values than moder extracts.

Discussion

It is clear from the results that not only is there a difference in the rate of disappearance of sub-samples of the same leaf litter placed in nylon hair-nets on mull and moder sites, but also a marked difference in the changes in composition. A visual comparison of the litter in the nets with the unconfined material of the natural litter layer showed that they both disappeared at a similar rate, with the possible exception of the tough and bulky leaves of oak on mull which were not easily removed from the nets by earthworms. Removal of solid material, whether by biological or physical agency, is only one of the processes causing loss of material from the nets. In addition, loss can occur through solution or production of gaseous or volatile compounds, all of which may result in changes in the composition of the litter. It is important to note that the material remaining in the nets is a relatively stable residuum of the original sample.

The loss of ash litter on the mull site is due mainly to the activity of large invertebrates especially earthworms; this is shown by the loss of whole leaflets from the nets and by the stripping away of the leaflet laminae. The contention that removal of solid matter is the major form of loss of ash litter on mull is supported by the chemical analyses. The C/N ratios of the ash litter remaining on mull (Table 2) show only slight variation after the first month, a reflection of the fact that the rates of loss of nitrogen and dry weight are very similar (Fig. 2). This suggests that for most of the time there is indiscriminate loss of material rather than the differential removal of particular major chemical components. On the other hand, during the first month, differential loss did occur; the results of water extraction suggest that solution was the prime cause of loss during this period. Analysis of freshly-fallen ash leaves demonstrated the presence of a hot-water-soluble component amounting to about 32 per cent. of the dry weight; after 1 month in the field this fraction had fallen to about 1·5 per cent. The water-soluble component of ash litter on moder shows a fall of similar magnitude over this period whilst the water-soluble fraction of oak litter on moder shows a more gradual decline (Fig. 3); the oak litter on mull was not analysed for total water-soluble material. Unlike any of the extracts from ash litter, the initial extracts from oak litter had the ability to precipitate gelatin from solution. As the gelatin-precipitating materials were probably polyphenolic compounds of high molecular weight it is possible that some of them were adsorbed on the filter paper during filtration. The negative results in these tests are therefore an indication of either the absence of water-soluble gelatin-precipitating materials in the litter or the presence of such compounds in amounts small enough to be completely adsorbed on the filter paper. The possible pedological aspects of protein precipi-

tation by leaf extracts have been explored by Handley (1954). As mentioned above, the cold-water extracts of neither oak litter nor ash litter gave positive reactions for the presence of protein.

The most unexpected result of the experiment is the increase in the absolute amount of nitrogen in the oak litter on moder to about 160 per cent. of its original value during the first 10 months. Whatever the cause of this increase it should be borne in mind that it must be due to nitrogen being added to the litter, not merely a differential loss of nitrogen-poor components. A possible source of the nitrogen is animals invading the litter. The very small animals are not removed during sorting, and prominent among these are nematodes. Using the maximal figures of nematode populations in oak litter from Roudsea Wood (D. C. Twinn, unpublished) and the estimate that 300,000–1,000,000 live nematodes weigh approximately 1 g. (based on Overgaard Nielsen, 1949) it is calculated that the nitrogen in this component could not account for more than 5 per cent. of the 60 per cent. increase, even if all the nematodes which were counted had migrated into the leaves from outside the nets. The actual contribution of the nematodes to the increase must be much smaller and indeed it seems unlikely that the total fauna left in the sorted samples, nematodes included, represents a large fraction of the 'new' nitrogen. Similarly animal excretory products are unlikely to be important in this respect. Saitô (1957) has demonstrated a similar increase in beech litter during the course of decomposition but he does not suggest a possible cause. Microbial fixation of nitrogen has been shown to occur in fallen oak leaves by Olsen (1932), but whether this process is involved here is unknown. The relatively low pH of the oak litter argues against fixation by bacteria. It is possible that nitrate-N and ammonia-N in the rain may be incorporated into microbial protein, but even if this is true an explanation has to be provided for the difference in the level of nitrogen in oak litter on the two sites. Tamm (1953) suggested that acidic materials in moss leaves may facilitate the uptake of ammonia from the air. In a similar way litter may absorb ammonia. These are all only tentative suggestions; the actual origin of the exogenous nitrogen and its mode of incorporation into the litter must await investigation.

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POLYPHENOLS IN PLANT, HUMUS, AND SOIL

I. POLYPHENOLS OF LEAVES, LITTER, AND SUPERFICIAL HUMUS FROM MULL AND MOR SITES

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Summary

The polyphenols of fresh green and dried leaves, litter, and superficial humus from mull and mor sites were examined by paper chromatography and paper electrophoresis. The greatest diversity and quantity of phenolic substances obtained in the extract of the fresh beech leaves from the mor site. There was a change in quantity of simple polyphenols grading from a maximum in fresh growing green leaves, falling through senescent leaves to dead leaves to fresh fallen leaves, to a minimum in decayed leaves and humus or stored dry leaves. Tannin stripping and especially hydrolysis and reduction of the decayed leaves and superficial humus released polyphenolic substances. The role of polyphenols in mull and mor formation is discussed.

Introduction

POLYPHENOLS are often present in leaves (Bate-Smith and Lerner, 1954). This is of considerable commercial importance in tea leaves (Roberts *et al.*, 1956), in bark (White *et al.*, 1952), and in tobacco (Mikailov, 1958).

It is also probable that they play an important role in processes concerned with the development of soil profiles. They have been studied in connexion with the transport of iron in freely drained soils (Bloomfield, 1957), the formation of humic acid (Flaig, 1955; Swaby, 1958), and some of the differences between mull and mor humus (Handley, 1954).

The range of polyphenols and their fate both within the plant and after release from it are conditioned by soil reaction. The present study was planned to examine polyphenols and their products in leaves, litter, and humus from typical mull and mor sites. Much of the work was done on beech (*Fagus sylvatica*), since it will grow in extremes of base-rich or base-deficient soils with the consequent formation in the one case of mull humus and in the other of mor. The effect of polyphenols in reducing and transporting iron is to be reported later, their role in humic acid formation has been considered elsewhere (Davies *et al.*, 1957; Coulson *et al.*, 1960).

Experimental

Mull sites

Knightwood Inclosure, New Forest, Lyndhurst, Hants, 200 ft. O.D. Brown Earth on Barton Sand.

Penrhyn Park, Llandegai, Caernarvonshire, 100 ft. O.D. Brown Earth on mainly shale drift.

Pistyll, Nercwys, Mold, Flintshire, 500 ft. O.D. Brown Earth on mixed Carboniferous Limestone and Millstone Grit drift.

Mor sites

Lodge Wood, Gt. Hampden, Bucks. Low Base Status Brown Earth (Micro-Podzol) on sands and gravels of Reading Beds.

Mynydd Du, Nercwys, Mold, Flintshire, 1,000 ft. O.D. Podzol on Millstone Grit.

Knightwood Inclosure, Lyndhurst, Hants, 200 ft. O.D. Podzol on Barton Sand.

Materials

Dried

Beech litter and surface humus (mull site, Knightwood; July 1957).

Beech humus (mor site, Knightwood; July 1957).

Green leaves on cut beech branches, surface litter of beech and of Japanese larch and the top 8 in. of humifying debris (mull site, Penrhyn Park, November 1957).

Beech humus (mor site, Lodge Wood, December 1957).

Fresh

Freshly fallen leaves: Beech, sycamore, and oak (mull site, Llandegai, October and November 1957; mor site, Beech, Penrhyn Wood, nr. Moel Wnion, December 1957).

Senescent leaves (mull site, Llandegai, November 1957).

Green beech leaves (mull site, Pistyll, Nercwys, June 1958; mor site, Mynydd Du, Nercwys, June 1958).

Before 17 November 1957 all samples were dried at 25° C. for 3 days, ground, and stored in the dark. Later it was suspected that polyphenols were being lost during the drying, so subsequently all samples were preserved in polythene bags by freezing at −20° C. Those collected at Nercwys (50 miles from Bangor) were frozen in liquid air during collection and then stored at −20° C.

Extraction of polyphenols

Techniques, of three general types, were used in this order:

(*a*) Extraction of free polyphenols by solvents.
(*b*) Extraction of combined polyphenols by 'tannin stripping' solvents (Gustavson, 1956).
(*c*) Extraction of simple phenolic substances released by 'chemical' methods (e.g. hydrolysis and reduction of polymers by electrolytic methods; cf. Smith, 1958).

Solvent extraction

The samples (1 g. to 200 g.) were either ground and then extracted by shaking with the solvent (5 ml. to 20 ml./g.) or were macerated with the solvent in a top drive macerator and left to stand for several hours before filtering.

The solvents were:

(*a*) ethyl acetate (laboratory temperature and +4° C.);
(*b*) methanol (+4° C.);

(*c*) 80 per cent. ethanol (v/v; laboratory temperature);
(*d*) acetone/water (1 : 1 v/v; laboratory temperature);
(*e*) cold water and hot water (refluxed for 45 min.) (5 ml./g.). The hot water filtrate was washed with chloroform to remove chlorophyll (but with some loss of flavonols). The solvent extracts were then each evaporated *in vacuo*. (In later experiments nitrogen was passed through the apparatus.)

'Tannin-stripping' solvents

(*a*) Powdered samples were left in 8 M urea solution (10 ml./g.) for 2 weeks. The solution was covered by ethyl acetate and a drop of toluene.
(*b*) Methanol/water mixture (3/2, v/v) was used in a reflux extraction (6 hours) (approx. 15 ml./g.).
(*c*) Acetone/water (1 : 1) as in (*b*) (4 ml. to 8 ml./g.).

'Chemical' methods

(*a*) *2 N hydrochloric acid treatment.* The sample was heated on a water bath with the hydrochloric acid (20 ml./g.) for at least 30 min. (preferably 60 min.) and then filtered. An *iso*-amyl alcohol (4 ml./g. samples) extract of the filtrate was then evaporated *in vacuo* to one-tenth of its original volume.

(*b*) *A Zeisel procedure.* The sample was heated with a hydriodic acid (s.g. 1·94)—water mixture (80/20, v/v) at 150° C. on an oil bath for 1 hour (8 ml./g.). During the heating, volatile organic iodides were blown away by a current of nitrogen. The cooled digest was filtered. The filtrate residue remaining after vacuum evaporation was extracted with water. This was washed with carbon tetrachloride to remove iodine, then methanol was added (3 : 2), and the mixture refluxed (1 hour). The evaporated residue was extracted with ethanol and the solution reduced to small bulk.

(*c*) *Hydrolysis and reduction.* 6 N hydrochloric acid hydrolysis in a sealed tube (100°, 24 hours) (6 ml./g.) was followed by electrolytic desalting and simultaneous reduction (Smith, 1958).

Paper electrophoresis

The apparatus and technique was the same as that used by Coulson and Evans (1958). A horizontal electrophoresis tank, Whatman No. 1 paper and M/40 borax buffer (500 V; 10 hours).

Paper chromatography

All the extracts were subjected to two-dimensional paper chromatography (Cartwright and Roberts, 1954*a*).

Paper: Whatman No. 4, 17 in. by 17 in. or 18¼ in. by 22½ in.
First solvent: *n*-butanol/acetic acid/water (4/1/2·2 v/v).
Second solvent: acetic acid/water (2 per cent. acetic acid).

Methods of detection

Reagent for general detection of polyphenols. For this purpose spots on the chromatograms were detected by dipping in a mixture of 1 per

cent. $FeCl_3$ and 1 per cent. $K_3[Fe(CN)_6]$ (Kirby, Knowles, and White, 1953).

Specific reagents for polyphenols. Some were dip reagents, others were sprayed on and the paper dried at 100° C. to develop the colour (i, Roux, 1957; ii, iii, iv, Cartwright and Roberts, 1954*b*; v, Coulson and Evans, 1958).

(i) *Three per cent. toluene sulphonic acid in ethanol.* This spray reveals leucoanthocyanins, flavan-3:4-diols, 2:3 dihydroflavanols, resorcinol, catechol, catechins, and phloroglucinol.

(ii) *Vanillin-p-toluene sulphonic acid.* This spray reveals catechins and leucoanthocyanins.

(iii) *Ethylenediamine.* This spray reveals gallic acid, theogallin, and galloyl derivatives.

(iv) *One per cent. potassium cyanide.* This dip reveals gallic acid and theogallin.

(v) *Sodium molybdate.* This spray reveals ortho-dihydroxy groups.

Other spray or dip reagents used were Folin and Ciocalteau (1927), diazotized *p*-nitraniline (Evans *et al.*, 1949), diazotized sulphanilic acid (Evans *et al.*, 1949), and silver nitrate (Smith, 1958). The chromatograms were also examined in ultraviolet light for fluorescent areas.

Estimation of polyphenols

The indigo-carmine method (Spiers, 1914) was used to obtain an approximate figure for the amounts of polyphenols present in fresh beech leaves from both mull and mor sites (Nercwys, June 1958).

Leucoanthocyanin reaction (Bate-Smith and Lerner, 1954)

The levels of leucoanthocyanin in the same fresh beech leaves were assessed by heating with HCl and extracting the colour so produced into *iso*-amyl alcohol.

Results

The greatest diversity and quantity of phenolic substances obtained in the extract of fresh beech leaves from a mor site (Nercwys, June 1958). A tracing of the chromatogram is given in Fig. 1.

Other extracts contained fewer kinds and less quantity of phenolic compounds, but more of the streaks which possibly may arise from more complex substances. In certain cases other spots appeared when the fresh leaves were dried or aged (Fig. 2). Fresh beech leaves from mull sites had fewer polyphenols (including leucoanthocyanins) in less quantity (Fig. 3).

The humified materials yielded very little polyphenol material on normal solvent extraction (e.g. with ethyl acetate) (Fig. 4), although a few more phenolic substances were obtained from mor litter and mor humus using a 'tannin-stripping' solvent (methanol/water) (Figs. 5 and 6).

The presence, in addition to the simple polyphenols, of oxidized and polymerized phenolic substances was demonstrated in both mull and mor partially humified materials by chromatography after acid hydrolysis and electrolytic reduction (Fig. 7).

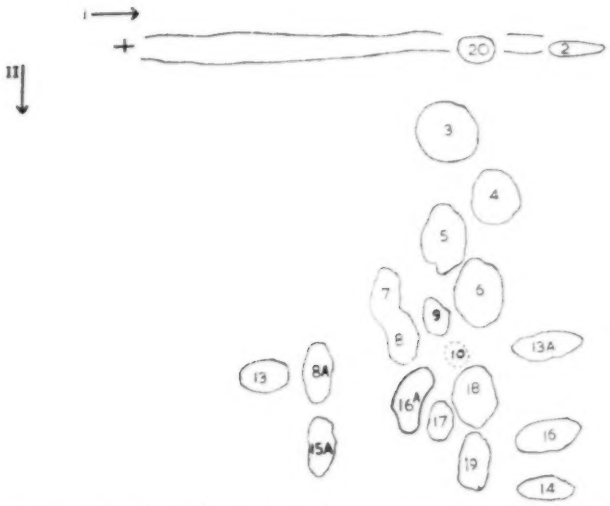

FIG. 1. Two-dimensional paper chromatogram of polyphenols in the ethyl acetate extract of fresh green beech leaves (mor site). Detection: $FeCl_3/K_3[Fe(CN)_6]$ (tracing). For key, see Table 1.

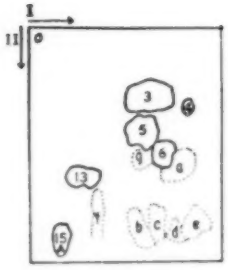

FIG. 2. Two-dimensional paper chromatogram of polyphenols in the ethyl acetate extract of green beech leaves (mull site; stored at −20° C.; aged during storage). Spots *a–g* had indistinct contours (tracing). For key, see Table 1.

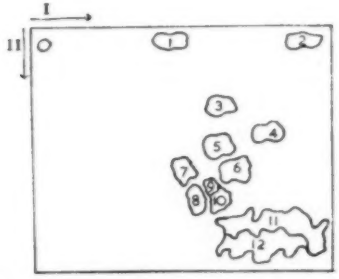

FIG. 3. Two-dimensional paper chromatogram of polyphenols in the ethyl acetate extract of fresh beech leaves (mull site). Detection: $FeCl_3/K_3[Fe(CN)_6]$ (tracing). For key, see Table 1.

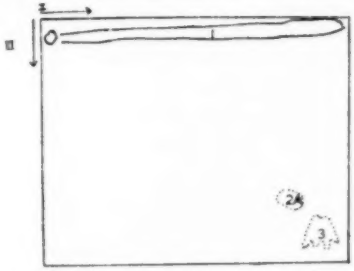

FIG. 4. Two-dimensional paper chromatogram of polyphenols in methanol, 80 per cent. ethanol, ethyl acetate, and urea extracts of humus and litter from mull and mor sites. Detection: $FeCl_3/K_3[Fe(CN)_6]$ (composite tracing). For key, see Table 1.

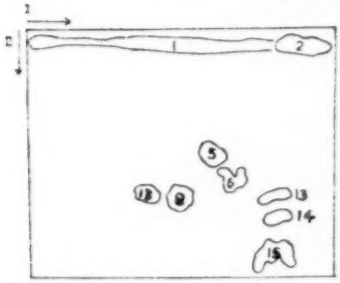

FIG. 5. Two-dimensional paper chromatogram of polyphenols in extract of fallen leaves (mor site) after refluxing with a methanol/water mixture ('tannin stripping'). Detection: $FeCl_3/K_3[Fe(CN)_6]$ (tracing). For key, see Table 1.

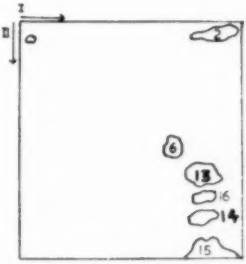

FIG. 6. Two-dimensional paper chromatogram of polyphenols in humus (mor site) after refluxing with a methanol/water mixture ('tannin stripping'). Detection: $FeCl_3/K_3[Fe(CN)_6]$ (tracing). For key, see Table 1.

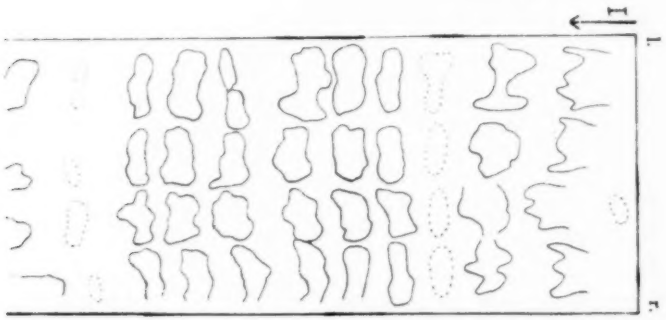

FIG. 7. One-dimensional paper chromatogram of polyphenols in reduced acid hydrolysates. Detection: $FeCl_3/K_3[Fe(CN)_6]$. Left to right: mull humus; mor humus; mor leaves (litter); mull leaves (litter) (tracing).

The Zeisel procedure, although a form of hydrolysis and reduction, did not release many kinds of polyphenols. The few that did appear were in fair quantity (Fig. 8).

The presence of a complex mixture of catechins, flavonoids, and other polyphenols is indicated by these reagents as well as by paper chromatography (Table 1). Detailed observations on the reaction of these and various phenolic substances have been given elsewhere (Lewis, 1958).

Fresh beech leaves from trees growing on mull and mor sites (Nercwys, June 1958) had distinct differences in polyphenol content. The aqueous extract of leaves from mor sites was twice as rich as that from mull sites

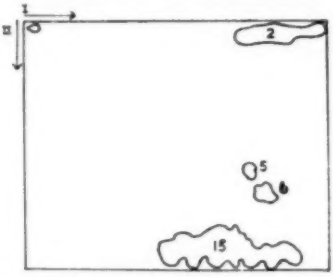

FIG. 8. Two-dimensional paper chromatogram of polyphenols in a reduced hydrolysate (Zeisel procedure) of humus and litter. Detection: $FeCl_3/K_3[Fe(CN)_6]$ (composite tracing). For key, see Table 1.

while the comparable ethyl acetate extract was six times stronger for mor than for mull.

In mor samples there is more glucosamine and more hydrolysable carbohydrate material than in mull (Lewis, 1958). The higher level of glucosamine may indicate greater fungal activity (and thus fungal chitin); whilst the higher level of carbohydrate material probably results from the 'masking' of cellulose by tanned protein (Handley, 1954).

Discussion

In attempting to appreciate the diversity of problems relating to mull and mor formation and to transportation of iron and other metallic elements in soil profiles, the role of polyphenols has been investigated.

Results, so far, are tentative, and work is still in progress, but having regard to the experience of Bloomfield (1957), Handley (1954), and others, they are not inconsistent with the following observations:

1. Beech leaves growing on base-deficient sites are richer in simple polyphenols (kind and quantity) than those growing on base-rich sites.

2. The polyphenols of fresh fallen leaves and presumably those in raindrops from growing leaves will, to some extent, be converted to more complex substances at the soil surface; this tendency is much more likely in base-rich than in base-deficient soil.

3. Humus collected from under beech is relatively deficient in free

polyphenols, but by tannin stripping methods, more could be released from both mull and mor materials, most being released by hydrolysis and reduction.

4. The same diversity of complexed and altered polyphenols is released from both mull and mor sites.

TABLE 1

Key to Figs. 1–7 with RF Values and Provisional Identification of Phenolic Substances in Leaves, Litter, and Humus. The Numbers are Standard Throughout (RF^1 = RF in Butanol/Acetic Acid/Water (4/1/2·2) (Solvent I). RF^2 = RF in Aqueous 2 per cent. Acetic Acid (v/v)) (Solvent II).

Spot no.	RF^1	RF^2	*Comments*
Streak	0–1	0	(*a*) RF^1 0·2–0·5. Leuco-anthocyanins probably as combined molecules. (*b*) RF^1 0–1. Catechin type polymers. (*c*) Possibly flavones, flavonols, or other planar molecules.
1	0·46	0	Flavone or flavonol.
2	0·89	0	Kaempferol or other yellow flavonol or flavone.
3	0·63	0·17	Unknown pigment.
4	0·74	0·31	Unknown.
5	0·62	0·36	*Epi*-catechin.
6	0·70	0·47	*D*-catechin.
7	0·53	0·51	Possibly galloyl derivatives of leuco-anthocyanins.
8	0·56	0·58	As 7.
8A	0·41	0·65	Possibly kaempferol-3-rhamnodiglucoside.
9	0·62	0·54	A leuco-anthocyanin.
10	0·68	0·59	As 9.
11	0·73	0·79	Unknown.
12	0·75	0·89	Unknown.
13	0·30	0·65	Unknown.
13A	0·84	0·59	Unknown.
14	0·84	0·87	Unknown.
15	0·80	0·89	Unknown.
15A	0·41	0·79	Unknown.
16	0·84	0·70	Unknown.
16A	0·84	0·76	As 7.
17	0·64	0·70	Leuco-anthocyanins.
18	0·70	0·68	Galloyl derivative of catechin.
19	0·69	0·84	Unknown.
20	0·71	0	Unknown (? planar structure).

It is fairly clear from our experience in this project that the materials under discussion are subject to alteration as the season progresses and that this alteration continues after the leaves are shed.

Any work on the influence of the polyphenols of any one site must recognize the change in quantity of simple polyphenols grading from a maximum in fresh growing green leaves falling through senescent leaves to dead leaves to fresh fallen leaves, to a minimum in decayed leaves and humus, or stored dry leaves.

It is possible that some of the anomalous results that puzzled earlier workers could be resolved if due regard were paid to changes consequent on this lack of stability of the polyphenols, e.g. changes that might be

imposed by methods of drying for storage, by methods of extraction, and by methods of isolation.

The resistance of simple polyphenols to oxidation and polymerization is well known to be greatest under acid and least under alkaline conditions. Base-deficient soils should then give just those conditions both for a higher yield of and a longer life for simple polyphenols.

The quantity of simple polyphenol reaching the soil may be at its maximum in spring and early summer rather than at the time of falling of senescent leaves, because rain showers will constantly remove polyphenols by dialysis from the growing leaves or from exudates on the leaf surface. The fate of this polyphenol at the soil surface will depend largely on the soil reaction. The role of these substances in the movement of iron in soil profiles will be the subject of a later paper.

While profile development may depend on polyphenols readily lost from the plant, the fate of leaf nitrogen would be more closely related to the kind and quantity of polyphenols remaining within the plant. Two processes may act concurrently. On the one hand, the polyphenols may form complex structures by a bridging with basic nitrogen-containing groups. On the other, polyphenols, if of the correct molecular range of size, may act as tanning agents capable of preserving protein from rapid decay.

Under base-rich conditions there is a greater chance of polymerization of the polyphenols beyond the size capable of tanning. In this connexion we have observed that polyphenols extracted from senescent beech and oak leaves of mor sites are capable of tanning gelatin more readily than similar leaves from a mull site.

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POLYPHENOLS IN PLANT, HUMUS, AND SOIL

II. REDUCTION AND TRANSPORT BY POLYPHENOLS OF IRON IN MODEL SOIL COLUMNS

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Summary

The two pure polyphenols, D- and *epi*-catechin, known to be present in the fresh green leaves of a number of tree species, have been shown to be capable of reducing ferric iron, in the form of hydrated ferric oxide, to an organic ferrous complex and solubilizing it in much the same way as do Bloomfield's leaf extracts. These polyphenols can remove iron, even when held firmly as in Triassic sand, and transport it as ferrous iron at low pH. Model soils, consisting of alumina and diatomaceous earth impregnated with ferric chloride, were treated with catechin solutions and fresh green-leaf extracts. Both produced dark coloured bands in which substantial amounts of ferric iron had been converted to ferrous iron. Extracts of green beech leaves from a mor site were more effective than those from a mull site (June leaf collection). Extracts of humus and litter were singularly low in reducing and iron-complex-forming substances, corresponding to their low free polyphenol status.

The illuvial horizon of a podzol formed on Barton sand has yielded organic matter on extraction with acetyl acetone. This contained much material of polyphenol origin associated with iron.

The role of polyphenol activity towards iron is discussed in relation to podzolic and other soils.

Introduction

LEACHED soils, i.e. where the rainfall is in excess of the potential evaporation and drainage is free, are characterized by the presence of free iron oxide and hence a brown colour. This condition ranges from the brown earth through the various podzolic soils to the podzol itself. The podzol is perhaps the soil which best serves to focus attention on the movement of iron because of its marked zonation. Bloomfield's (1957) studies over the last years have suggested that polyphenol complexing, with the aid of acids, is at the heart of the reduction and transport of iron. That levels of polyphenol in leaves differ according to whether the site is of mull or mor, as suggested by Handley (1954), has been supported by fresh evidence (Coulson *et al.*, 1960 *a*). It is probable too that different species contain different kinds and amounts of polyphenols. Our experience has shown that the polyphenols D- and *epi*-catechin occur commonly in the leaves of tree species and they were therefore chosen for the valuation of iron movement.

Experimental

Tube reductions

(i) *Series.* Three sets of three tubes, one for each buffer, were made up, each tube containing polyphenol (0·1 g.), ferric oxide (0·5 g.), and buffer (25 ml.). Each set had three tubes, one that stood in the laboratory, another in a vacuum desiccator filled with nitrogen, and a third through

which air was drawn continuously. There were two parallel series, one for D-catechin, the other *epi*-catechin.

(ii) *Tubes.* Boiling tubes (6 in. by 1 in.) were enclosed in black paper and fitted with stoppers covered with Polythene.

(iii) *Ferric oxide.* Hydrated ferric oxide was prepared by mixing solutions of ferric chloride and ammonia (2 N). The precipitate was filtered by suction and washed first with very dilute ammonia, then with water. By standing in a desiccator overnight the ferric oxide was partially dried.

(iv) *Buffers* (Vogel, 1953). pH 3·72, pH 5·89 (sodium acetate–acetic acid) and pH 12·38 (calcium hydroxide-sodium chloride) (Strouts, *et al.*, 1955).

(v) *Polyphenols.* D-catechin (Lights and Co.), *epi*-catechin (kindly supplied by the late Dr. R. Bradfield).

(vi) *Estimation of ferrous ion* (cf. Snell and Snell, 1949). Portions (1 ml.) were diluted with a little distilled water, then mixed with 10 per cent. H_2SO_4 (1 ml.), 25 per cent. H_3PO_4 (1 ml.), and 1 per cent. solution of α,α'-dipyridyl in 0·7 per cent. aqueous HCl (0·4 ml.), and 20 per cent. ammonium acetate (10 ml.). The mixture was made up to 100 ml. with distilled water, and allowed to stand overnight in the dark. The colour which developed during the slow release of ferrous iron from its complex was then measured by an 'EEL' photoelectric colorimeter (green filter; No. 625). The colour of cobalt nitrate in water was used as a comparison (1·235 g. cobalt nitrate hexahydrate in 100 ml. ≡ 0·162 mg. ferrous dipyridyl/100 ml.). Blank tests were carried out on the polyphenols in aqueous solution.

Paper electrophoresis

Electrophoresis was applied to (*a*) tube reduction products, and (*b*) leachings, from columns (1), (2), and (3) of the Triassic-sand experiment, evaporated *in vacuo* to small bulk.

Method. The method has been reported (Coulson and Evans, 1958). For the tube reduction products (*a*), samples (51 days and 98 days) from some of the D-catechin ferric oxide pilot experiments were applied as spots on Whatman 3 MM paper and run for 5 hours at 600 V in M/40 sodium borate buffer. Of the column leachings (*b*) 2 ml. of the concentrate were run for 9 hours at 500 V.

Detection. The air-dry papers were sprayed with α,α'-dipyridyl solution and any pink areas were marked. They were then dipped in the $FeCl_3$–$K_3Fe(CN)_6$ reagent to locate phenolic spots (Cartwright and Roberts, 1954).

Paper chromatography

(*a*) *Ferrous ion.* Paper: Whatman No. 4. Development: one dimensional. Solvents: *A*: *n*-butanol/ethanol/water (8/5/5; v/v) (Stevens, 1956) or *B*: *n*-butanol/acetic acid/water (4/1/2·2; v/v) (Cartwright and Roberts, 1954).

Detection. After solvent A. The paper, after drying, was held over a boiling 8 per cent. solution of oxine. Oxine forms a grey-green complex with iron.

After solvent B. The paper, after drying, was sprayed with a mixture of 1 per cent. α, α′-dipyridyl solution (5 ml.), 20 per cent. ammonium acetate solution (5 ml.), water (10 ml.), dilute H_3PO_4 (1:4; 0·5 ml.), and 10 per cent. H_2SO_4 (0·5 ml.). A pink complex forms with ferrous iron.

Samples from the tubes with D-catechin and *epi*-catechin buffered at pH 3·72 (1 ml. in each case) were used for chromatography.

(*b*) *Polyphenols.* The two-dimensional method was that used earlier by Coulson *et al.*, 1960. The samples were from a D-catechin tube pilot experiment at pH 4·05 (sodium acetate–acetic acid) (1 ml.) and from columns (1) and (2) in the Triassic-sand experiment (1 ml. of the extract concentrated from 20 ml. to 2 ml.).

Column experiments

(i) *Triassic-sand columns.* Triassic red sand (Vale of Clwyd), washed with tap water to free it of clay, was poured into five cylindrical tubes (36 in. by 1¼ in.) which were filled with water so as to aid even packing. Glass wool layers below and above held the sand in position. The tubes were covered with black paper to exclude light and were held vertical. Various solids were put on top of the sand and they were leached through with solutions as follows:

	Solid	*Leaching liquid*
Column (1)	Polyphenols	Buffer solution pH 3·72
,, (2)	Polyphenols	Buffer solution pH 5·89
,, (3)	Polyphenols	Water (pH 5·2)
,, (4)	Blank	Buffer solution pH 3·72
,, (5)	Mor organic material	Water and mor extracts

D-catechin and *epi*-catechin (100 mg. each) were placed on the surface of the sand in columns (1), (2), and (3). Mor humus (64 g. previously stored at −20° C.) and fallen beech leaves (5 g.) collected from Lodge Wood, Hampden, Bucks., were packed on column (5). The columns were leached periodically with portions (50 ml.) of the appropriate buffer or water (see Table 1). Column (5) was leached with portions (50 ml.) of a filtered extract of humus (200 g.) prepared by refluxing with methanol-water. Following the leaching (300 ml. in all) hot air (100–150° C.) was drawn over the sand surface for 4 hours resulting in a drying of the surface of the sand and a sand temperature of 35–40° C. D-catechin (200 mg.) was added to columns (1), (2), and (3) and the cycle repeated. The leachings were collected and portions (20 ml.) analysed for ferrous iron by the α, α′-dipyridyl method, and portions (5 ml.) for aluminium (Chenery, 1948).

(ii) *Alumina and 'Celite 535' columns: examination of D- and epi-catechin.* 'Celite 535' (diatomaceous earth: Johns Manville) and alumina (80 g.) were poured into a series of glass tubes (16 in. by ¾ in.) in the form of a slurry with 4 per cent. ferric chloride solution. The supernatant liquid was drained off, and then the column in the tube was covered with a layer of acid washed sand.

Polyphenol solutions (20 ml. ≡ 150 mg. of polyphenol), containing

2 drops of glacial acetic acid to suppress initial colour formation, were poured down the columns:

(1) D-catechin Alumina.
(2) *Epi*-catechin Alumina.
(3) D-catechin 'Celite 535'.

The following day surplus liquid was drawn off, the column material expelled carefully with compressed air, and the bands cut out, together with a length (1 in.) from the base of the column which had not reacted. These band extracts (extraction with 20 ml. H_2O) were analysed for ferrous and ferric iron. The ferrous iron was estimated as before (in 1-ml. samples) and the ferric iron as follows (cf. Snell and Snell, 1949*a*).

Ferric iron. The sample (1 ml.) was gently evaporated to dryness over a bunsen flame. After cooling, hydrochloric acid solution (2 ml.–1:15) was added, the mixture shaken, then the α,α'-dipyridyl solution (2 ml.:0·1 g. of α,α'-dipyridyl dissolved in 1:15 HCl–H_2O) was also added. 10 per cent. sulphite solution (1 ml.) freshly made, was added and the tube allowed to stand for 1 min. Further sodium sulphite solution (2 ml.) was then added and the volume made up to 100 ml. After standing the solution for 1 hour, the colour produced was measured as before.

Other examinations. The remaining portion of each band was extracted with ethyl acetate (5×20 ml.) and the bulked extracts were evaporated *in vacuo* (to 2 ml.) and the concentrate examined for polyphenols by paper chromatography.

The effect of pH and 'ageing' on the reducing power of D-catechin was examined by pouring both fresh and 'old' D-catechin solutions (5 ml. original content of D-catechin:0·01 g.) mixed with water (5 ml.) and glacial acetic acid (2 drops) through prepared $FeCl_3$– 'Celite 535' columns (as used previously). The D-catechin solutions used were in distilled water, and in pH 3·72, pH 5·89, and pH 9·60 buffers (Vogel, 1953). After standing overnight, the complete banded areas formed were analysed for iron and polyphenols.

(iii) *Alumina and 'Celite 535' columns: examination of materials from mull and mor sites. Columns.* 'Celite 535' (70 g.) and alumina (80 g.) were stirred into separate ferric chloride solutions (17 g. ferric chloride in each 200 ml. portion) and tubes filled with the resultant slurries to form columns.

Extracts. Frozen beech leaves (−20° C.; 20 g. each, 1 week frozen) from mull and mor sites at Nercwys, Flintshire, were macerated with water (150 ml.) for 10 min. After filtering, glacial acetic acid (3 ml.) was added to each extract and the volume adjusted to 150 ml. The complete extract (150 ml.) was used for the alumina columns but much less extract (35 ml.) was used for the 'Celite 535' column. Green leaves from another mull site (Penrhyn Estate, Llandegai, Caerns.) and preserved for 8 months at −20° C.) were similarly extracted and used. Superficial humus (50 g.) (stored at −20° C.) and beech leaves (20 g.) from another mor site (Lodge Wood) as well as fallen beech leaves (20 g.) from a mull site (Penrhyn Estate) were extracted in a similar

fashion. Portions (35 ml.) of these solutions were poured through 'Celite 535' columns and the resultant system analysed.

Examination of B horizon

Material from the B horizon of a podzol formed on Barton sand under Scots Pine, Knightwood, New Forest, was used for the experiment.

(i) *Extraction with acetyl acetone* (cf. Martin and Reeves, 1957). B horizon material (100 g.) was extracted with 2 M acetyl acetone (600 ml.) by shaking for 2 hours. The residue of soil after extraction, the solid matter extracted, and the original B horizon soil were then compared with one another, for loss on ignition, carbon (Walkley–Black), nitrogen (Kjeldahl), aluminium (Chenery, 1948) and total iron after digestion (Snell and Snell, 1949*a*, *b*). The results are given in Table 6.

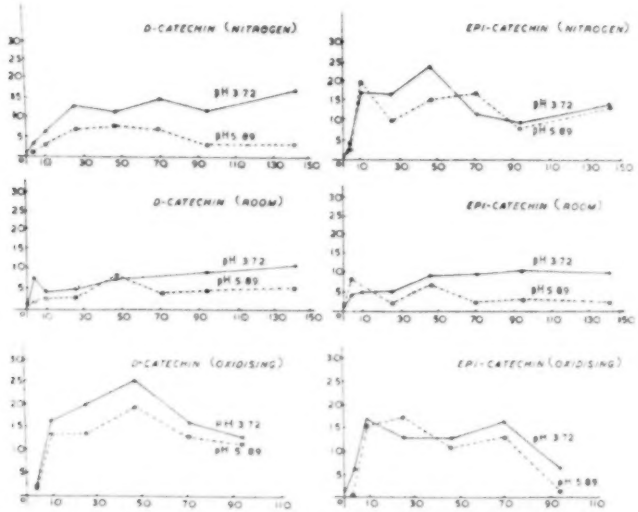


FIG. 1. Reduction of Fe^{3+} to Fe^{2+}. Results of tube experiments: (i) D-catechin in nitrogen; (ii) *epi*-catechin in nitrogen; (iii) D-catechin in room atmosphere; (iv) *epi*-catechin in room atmosphere; (v) D-catechin in presence of air bubbling; (vi) *epi*-catechin in presence of air bubbling. Solid line: buffer pH 3·72; broken line: buffer pH 5·89. Ordinate, mg. ferrous dipyridyl; abscissa, time (hours).

(ii) *Polyphenol content of the acetyl acetone extract.* The polyphenol content was found by hydrolysis of the solid extract (6 N HCl sealed tube, 24 hours at 100° C.) and subsequent estimation by the Folin and Ciocalteau (1927) reagent with D-catechin as standard. The hydrolysate was also examined by both one- and two-dimensional paper chromatography.

Results

Tube reduction. The course of reduction of hydrated ferric oxide in tubes is shown in Fig. 1.

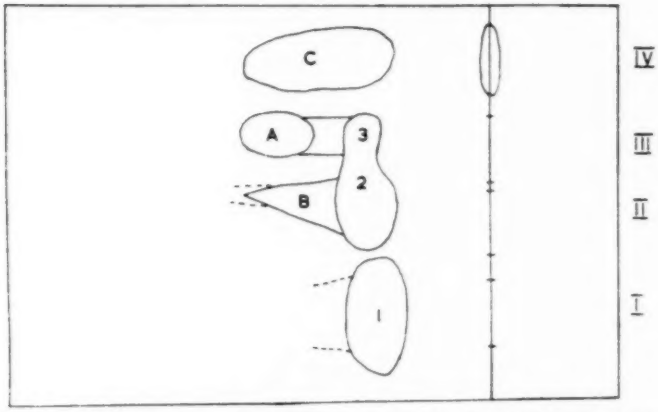


FIG. 2. Electrophoretogram of substances present in D-catechin solutions which have stood in contact with commercial ferric oxide for 51 days (Pilot experiment). Electrophoretogram developed by dipping in ferric chloride in potassium ferricyanide reagent. I, in buffer pH 4·05; II, in buffer pH 5·89; III, in water (pH 5·2); IV, extract of beech leaves from mull site: spot on starting line is ferric chloride-potassium ferricyanide positive (Tracings). 1, 2, 3, D-catechin; A, dark brown and strongly ultraviolet absorbent before dipping; B, light brown before dipping; C, pale brown before dipping. (Anode l.h.s.; cathode r.h.s.)

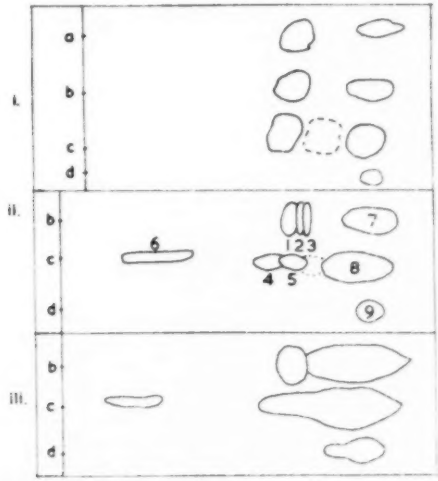


FIG. 3. Electrophoretograms of the solutions used in Fig. 2 but after 98 days (Pilot experiment). (Tracings.) (i) Detection by ferric chloride-potassium ferricyanide; (ii) appearance in daylight; (iii) detection by ultraviolet light (Chance OX7 filter); (*a*) D-catechin marker; (*b*) D-catechin in buffer pH 4·05 (cf. I, Fig. 2); (*c*) in buffer pH 5·89 (cf. II in Fig. 2); (*d*) in water (pH 5·2; cf. III in Fig. 2); 1, yellow band; 2, red band; 3, black band; 4, yellow band; 5, diffuse red band; 6, red streak, 7, yellow-brown area; 8, orange-brown area; 9, dark brown spot. (Cathode l.h.s.; anode r.h.s.)

The electrophoretic separation of substances present in D-catechin solutions which had been in contact with commercial ferric oxide for 51 days (pilot experiment) is to be seen in Fig. 2.

The result of a further electrophoretic examination after 98 days is shown in Fig. 3. With increasing pH the catechin is converted into faster migrating spots. In the water solution, without buffer, nearly all the catechin has disappeared and new substances are formed (Fig. 3).

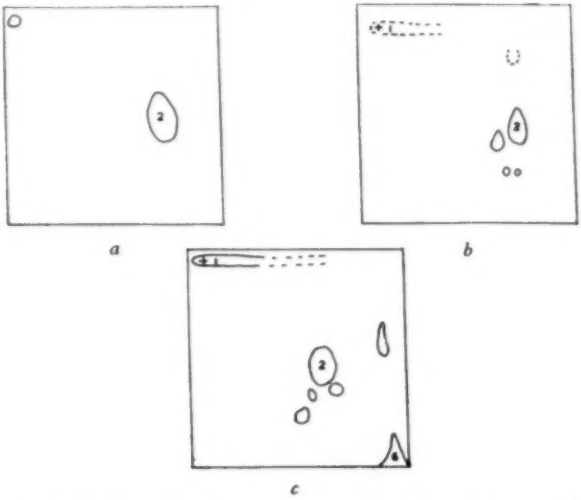


FIG. 4. Paper chromatograms of solutions used in Fig. 2 (tracing). Detection by ferric chloride-potassium ferricyanide. D-catechin (*a*) in buffer pH 4·05 (cf. I in Fig. 2); (*b*) in buffer pH 5·89 (cf. II in Fig. 2); (*c*) in water (cf. III in Fig. 2).

The chromatograms of polyphenolic substances present in the various D-catechin solutions which had been left in contact with hydrated ferric oxide (pilot experiment) are given in Fig. 4.

The amount of D-catechin remaining in each solution is indicated by the strength of spot no. 2 and is in the order: pH 4·05 > H_2O ⩾ pH 5·89.

The solutions examined were those from a pilot experiment. The phenol streak no. 1 and spot no. 6 are found to occur in many of the polyphenol extracts of beech (Fig. 4*c*). The conversion of D-catechin to other polyphenolic substances appears to be least in the pH 4·05 buffer (Fig. 4*a*).

Triassic-sand columns. The amounts of Fe^{+++} and Al^{++} leached from columns of Triassic sand by polyphenol solutions, mor organic matter extracts and by water and by the acid buffer alone are given in Table 1. The polyphenol leaching at pH 3·72 removed ten times more Fe^{++} than the pH 3·72 buffer without polyphenol, and five times more than either polyphenol leachings at pH 5·89, pH 5·2 (distilled water), or leaching through organic matter alone. The leaching did not really differ significantly between polyphenol solutions at pH 5·89 and pH 5·2 (distilled

TABLE I

(a) Reduction and Movement of Iron in Triassic-sand Columns. The Average Amount Moved in 60 Days of Leaching (50 ml. leachate) (Ferrous Iron: Ferrous Dipyridyl, mg./100 ml.; Aluminium: mg./ml.)

	Fe^{2+}					Al^{3+}				
Column no.	1	2	3	4	5	1	2	3	4	5
Amount (mg./ml.)	8·41	1·57	1·39	0·85	1·26	0·403	0·092	0·058	0·441	0·051
Standard error	1·02	0·41	0·47	0·41	0·30	0·008	0·005	0·001	0·006	0·001
Number of determinations	22	22	22	22	22	14	14	14	13	13

(b) Column comparisons

Fe^{2+}										Al^{3+}					
1–2	*1–3*	*1–4*	*1–5*	*2–3*	*2–4*	*2–5*	*3–4*	*3–5*	*4–5*	*1–2*	*1–4*	*2–3*	*2–4*	*2–5*	*3–5*
S $P<0·001$	S $P<0·001$	S $P<0·001$	S $P<0·001$	NS $P>0·05$	S $P<0·001$	NS $P>0·05$	S $0·01>P>0·001$	NS $P>0·05$	S $0·05>P>0·01$	S $P<0·001$	NS $P>0·05$	NS $P>0·05$	S $P<0·001$	S $0·05>P>0·01$	NS $P>0·05$

NS = Not significant; S = Significant at $P = 0·05$.

water) and mor organic matter extract. The movement of aluminium appeared to be completely independent of polyphenol, but was the more

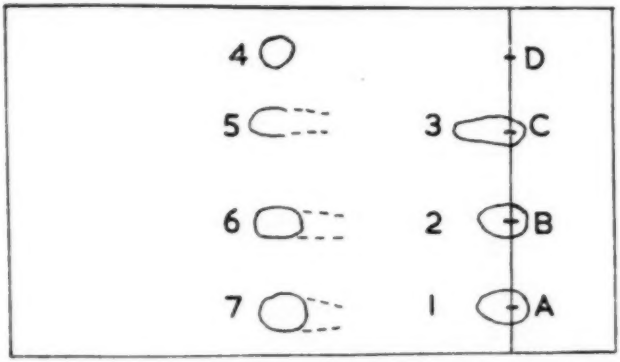


FIG. 5. Electrophoretogram of the concentrated effluents from the columns leached with D-catechin solutions (in pH 3·72 and pH 5·89 buffers; water at pH 5·2). D-catechin (A) in pH 3·72 buffer; (B) in pH 5·89 buffer; (C) in water (pH 5·2); (D) D-catechin marker. α,α′-dipyridyl detection (for ferrous iron) gives 1, strongly positive; 2, negative; 3, weakly positive. Ferric chloride-potassium ferricyanide detection (polyphenolic substances) 4–7, positive.

effectively extracted the lower the pH. The pH 3·72 buffer was the most effective extractant used.

Chromatograms of the concentrates of the solutions from the column leached with polyphenol (pH 3·72 buffer) showed discrete polyphenolic spots similar to those in Fig. 4*a*. By contrast those from leaching at pH 5·89 had only material with high R_F values (probably polymers) in both solvents.

The electrophoretogram of the concentrates from the pH 3·72, pH 5·89, and water columns is given in Fig. 5. Spot no. 1 (polyphenol leaching at pH 3·72) gave a strong positive for ferrous iron with α, α′-dipyridyl; spot no. 2 gave a weak positive with the reagent (cf. results in Table 3 (ii)). The ferrous iron thus appears to be present in a complex form possessing no residual electric charge. Spots 4 to 7 were detected with the $FeCl_3$–$K_3(Fe(CN)_6)$ reagent.

Ferric chloride treated alumina and 'Celite 535' columns

Results (expressed as a ratio of ferrous to total iron) for the various bands formed when solutions of D- and *epi*-catechin in water were passed through the columns are given in Table 2. These show that the formation of the strongest bands is, as expected, associated with the largest proportion of ferrous iron. Two new phenolic spots (R_F 0·33 and 0·39 in the *n*-butanol/acetic acid/water solvent) appear in chromatograms of the ethyl acetate extracts of the bands where the ferrous to total iron ratio is highest (i.e. pH 3·72 and water solutions), the strength of the original polyphenol spot being much weaker.

Solutions of D-catechin, one in distilled water, others buffered at

pH 3·72, pH 5·89, and pH 9·6, all kept for 130 days, were compared in their banding activity with freshly made solutions of the same pH. Plate I illustrates the banding by the old solutions. Though these were not very different in appearance from bands produced by the fresh solutions, analyses (Table 3) show that the older, less acid solutions do not maintain the activity displayed by comparable fresh solutions, and the alkaline solutions lose activity very rapidly.

TABLE 2

(i) *Description of Bands Produced in Ferric Chloride Impregnated 'Celite 535' or Alumina Columns by D- and Epi-catechin Solutions*

Polyphenol	*Support*	*Band no.* 1	2	3	4
D-catechin	A	White layer: iron partly leached	Grey-green band	Dark-green band	Unchanged
Epi-catechin	A	Dark blue band	No apparent change	Narrow green band	Unchanged
D-catechin	C	White layer: iron partly leached	Brown band	Faint pink band	Unchanged

A, alumina; C, 'Celite 535'.

(ii) *Iron Analyses of the above Bands (Ferrous to Ferric Ratio given)*

Polyphenol	*Support*	% Fe^{2+}/Fe *Band no.* 1	2	3	4
D-catechin	A	80	100	100	17·5
Epi-catechin	A	18·7	88·7	27·7	24
D-catechin	C	100	37·8	3·8	0·4

A, alumina; C, 'Celite 535'.

Acidified aqueous extracts of fresh beech leaves from mull and mor sites were examined by this method. The mor samples produced bands with a higher ferrous to total iron ratio than did mull samples (Table 4).

The ability to produce bands with high ferrous to total iron ratio was found to be greatest in extracts of fresh leaves, especially from mor sites (June 1958). No real difference could be detected between the extracts of fallen leaves or humus whatever the site; all had little activity (Table 5). Chromatographic evidence, showing most polyphenols in fresh green leaves and least in humus (Coulson *et al.*, 1960*a*) is in harmony with this observation.

The B, illuvial, horizon of a podzol formed under beech on Barton sand, when extracted with 2 M acetyl acetone, showed that most of the C and N was brought into solution. A substantial portion (about 50 per cent.) of the organic matter so extracted is polyphenolic in origin (Table 6).

The material of the extract not accounted for as organic matter is probably fine clay carried through the filter in colloidal suspension.

TABLE 3

(i) *Description of Bands produced in Ferric Chloride Impregnated 'Celite 535' Columns by 'Aged' D-catechin Solutions (130 days; see Plate I)*

No.	Buffer pH	Band			
		a	*b*	*c*	*d*
1	3·72	White layer leached free of colour	Green	Brown	..
2	Water (5·2)	Brown	Green-brown	..	..
3	5·89	Grey-black	Brown	Green-brown	Red-brown
4	9·60	Grey	Green-brown	..	..

(ii) *Iron Analyses of the Upper (Altered) Part and Lower (Unchanged) Part of the Columns (per cent. Ferrous of Total Iron)*

Column no.	Buffer pH	% Fe^{2+}/Fe	
		Upper (changed)	*Lower (unchanged)*
1	3·72	97·5	1·6
2	Water (5·2)	38·2	0·6
3	5·89	18·6	0·7
4	9·60	14·4	0·4

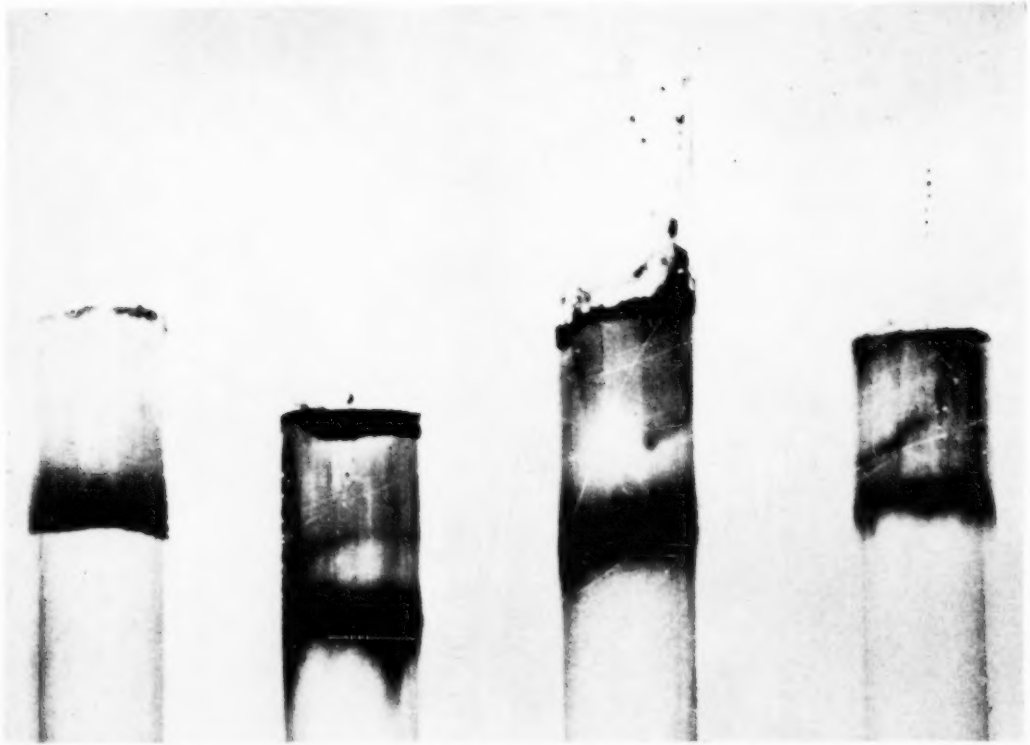
(iii) *Iron Analyses of Similar Columns where Fresh D-catechin Solutions were used (Calculated to Same Total Iron as* (ii))

Column no.	Buffer pH	% Fe^{2+}/Fe	
		Upper (changed)	*Lower (unchanged)*
1	3·72	92·5	2·74
2	Water (5·2)	68·9	2·59
3	5·89	55·3	3·47
4	9·60	19·5	3·76

Discussion

The identification of D- and *epi*-catechin as two of the major polyphenols of beech leaves (as well as of other species) (Coulson *et al.*, 1960*a*) led to their use for studies on the reduction and movement of ferric iron. The reduction experiments show that the catechins are capable of reducing iron (Fig. 1) and that a large range of colours in the solutions probably results from the formation of a series of iron-polyphenol complexes. There is paper electrophoretic (Figs. 2, 3, and 5) and paper chromatographic evidence that D-catechin acts with ferric iron to form ferrous complexes.

The experiments show that reduction by catechins varies with the conditions. After the first fairly rapid rise in ferrous iron complex in the solutions, the process is halted or in the case of aerated conditions,



The effect produced by passing an aqueous and buffered 130-day-old solution of D-catechin through columns of 'Celite 535' impregnated with ferric chloride. The columns are (reading l. to r.): 1, pH 9·6; 2, water (pH 5·2); 3, pH 5·89; 4, pH 3·72. [All solutions were slightly acidified with glacial acetic acid immediately before use.]

C. B. COULSON, R. I. DAVIES, *and* D. A. LEWIS—PLATE I

even reversed. Under this induced aeration the initially larger value for ferrous iron is probably caused by the agitation of the particles of hydrated ferric oxide and their thorough mixing with the catechin; the later fall in value could be due to the oxygenation brought about by thorough aeration.

TABLE 4

(i) *Description of Bands produced in Ferric Chloride Impregnated Alumina and 'Celite 535' Columns by Acidified Aqueous Extracts of Fresh Green Beech Leaves (Mull and Mor Sites)*

Column no.	*Leaf extract (site)*	*Support*	*Band*				
			a	*b*	*c*	*d*	*e*
1	Mull	A	Blue	Dark blue	Chocolate	Red-brown	..
2	Mor	A	Blue	Dark blue	Chocolate	Red-brown	..
3	Mull	C	Bleached	Brown	Dark green	Green	Unchanged
4	Mor	C	Bleached	Brown	Diffuse dark green	Green	Unchanged

A, alumina; C, 'Celite 535'.

(ii) *Iron Analyses of (1) Banded Region (2) Section of Bleached Area (columns 3 and 4) (3) Section from Base of Column (per cent. Ferrous of Total Iron)*

Column no.	*Leaf extract (site)*	*Support*	% Fe^{3+}/Fe		
			Section no.		
			1	*2*	*3*
1	Mull	A	24	..	10
2	Mor	A	44	..	30
3	Mull	C	44	35	0·7
4	Mor	C	61	38	5·7

Under slight acid or nearly neutral reaction, polyphenol changes to a multiplicity of complex phenolic products. This is confirmed by chromatography (Fig. 4) and is in accord with the accepted lowered stability of polyphenols with rise in pH. The change may proceed directly without involving the ferric oxide of the system, and having occurred, would account for the generally lower production of ferrous iron under such less acid conditions. The mechanism of polyphenol oxidation probably involves free radical participation (Hathway, 1958; Collison *et al.*, 1956; Cherniak *et al.*, 1958). The reduction of ferric iron to ferrous by polyphenols could be considered as follows:

$$R^1 \text{ (organic free radical)} + Fe^{3+} \rightarrow \text{stable product(s)} + Fe^{2+}$$

(Cherniak *et al.*, 1958).

Iron is mobilized by the action of polyphenols, especially in buffers of low pH, even when it is firmly held as in the case of red Triassic-sand grains (cf. Table 1). Yellow Barton sand, in which the iron is less firmly bound, yields even larger quantities of ferrous iron (Coulson, Davies and Lewis, 1960*b*). Since low pH buffer alone is not active, it would seem that the main movement is brought about by polyphenol. The

relative failure of polyphenol under less acid conditions is related to the contemporary production of more complex forms of the polyphenol which do not combine with iron (cf. Fig. 4) as well as to the lower Fe^{+++} concentration at the higher pH. Bloomfield (1957) points to the solubilization of iron by plant and litter extracts of a polyphenolic nature and also observes its more ready solubility in presence of acid.

TABLE 5

(i) *Description of the Effect produced in Ferric Chloride Impregnated 'Celite 535' (and in one case Alumina) by various Leaf, Litter, and Humus Extracts*

Column no.	*Leaf extract*	*Site*	*Support*	*Appearance*
1	Frozen green beech leaves, (−20° C.)	Mull	C	Bleached portion is followed by a narrow band then by unchanged lower regions. Some blueing at the surface, lower region unchanged.
1*a*	Stored for 1 year	Mull	A	Some blueing at the surface, lower region unchanged.
2	Fallen leaves	Mor	C	As in 1.
3	Fallen leaves	Mull	C	As in 1.
4	Humus	Mor	C	As in 1.

A, alumina; C, 'Celite 535'.

(ii) *Iron Analyses of (1) Banded Region, (2) Section at the Base of the Column (per cent. Ferrous of Total Iron)*

Column no.	*Leaf extract*	*Site*	% Fe^{2+}/Fe	
			1	*2*
1	Frozen green beech leaves (−20° C., stored 1 year)	Mull	30	7
2	Fallen leaves	Mor	6	2
3	Fallen leaves	Mull	8	5
4	Humus	Mor	2	2

The movement of aluminium did not appear to be influenced by the polyphenols used by us, but rather depended on acidity (Table 1). This does not exclude the possibility that other polyphenols may be active as, for example, the flavanoids, which are present in leaves and are known to form complexes with aluminium.

Rain washings of growing leaves contain polyphenols (cf. Bloomfield, 1957; Coulson, Davies, and Lewis, 1906*b*) and it has been pointed out that rain bearing these leaf washings may be an important source of polyphenol for the shift of iron in soil profiles (Coulson *et al.*, 1960*b*). Some indirect evidence of this emerges from a recent report by Kaurichev *et al.* (1958), where it is observed that the mobilization of iron is at a maximum in spring and early summer, a period coincident with

high values of polyphenols in green leaves. Swaine *et al.* (1959) have observed that, in leaf of the Victoria plum, free polyphenol reaches a maximum early on in the development of the mature leaf and maintains its value till senescence approaches during which it falls appreciably. It is of interest that Kaurichev *et al.* (1958) found that only organically bound iron free from ionic charge can travel down model profiles without interference by ion exchange. Our own experience on electrophoresis of iron-polyphenol complex—see earlier in the paper—suggests they would fulfil this condition. This is borne out by our model profile experiments.

TABLE 6

Results of Acetylacetone Extraction of a B Horizon (Podzol-Barton Sand; per cent. by Weight of Dry B Horizon)

Fraction	*Ignition loss*	*Carbon (Walkley and Black)*	*Total nitrogen (Kjeldahl)*	*C/N ratio*	*Total Fe*	*Total Al*	*Polyphenol in hydrolysate*
Original B horizon	5·39	2·41	0·17	14·1	0·50	0·072	..
Residue insoluble in 2M acetylacetone	1·43	0·55	0·09	6·1	0·26	0·016	..
Acetylacetone (2M) soluble material	5·82	1·71	0·12	14·3	0·20	0·017	1·45

The residual activity attributed to litter (cf. Bloomfield, 1957; and Kaurichev *et al.*, 1958) could be due to the simpler polyphenols washed by the rain from growing green leaves into the litter and not to the polyphenols present as complexes in the dead leaves forming the litter.

Fresh green leaf extracts, containing as they do appreciable amounts of polyphenols, are just as capable as D- and *epi*-catechin of producing leached and strongly reduced dark coloured zones in columns of alumina and 'Celite 535' impregnated with ferric chloride (Table 4, cf. Table 2 and Plate I). Concentrated leaf *in vivo* washings also possess this property (Coulson, Davies, and Lewis, 1960*b*). We have found polyphenols in the B horizon of a podzol and are investigating their form, quantity and mode of deposition.

In the case of the podzol a stage in the formation of the B horizon must admit of the reprecipitation of the iron-polyphenol complex. This would then be subject to some microbial alteration. There is ample evidence that both iron and polyphenol are abundantly present in a complexed form in this horizon for they can be abstracted by the standard procedures.

The activity of the polyphenols in the soil profile will depend not only on their abundance but also on the conditions under which they act. In the main they will be adversely affected by high pH and high temperature. It is not necessary to assume that an acid humus layer of organic matter is an essential prerequisite for podzolization; it is probably a concurrent feature and not the main cause. If this hypothesis is

accepted, then the occurrence of deep podzols in the tropics (see Mohr and van Baren, 1954) could be explained as a coincidence of high polyphenol fresh leaf leachate from tropical vegetation, with quartzose parent material subject to high rainfall.

Equally, too, the gap between podzols and brown forest soils would disappear. The marked coloration of low base status soils under oak woodland, for example, would simply be a reflection of the high degree of mobilization of iron by leaf polyphenols coupled with the mixing of the soil by earthworms. This tendency would become less as the soil acidity lessens and would afford a natural explanation of the lack of imposed brown colour in high base status soils.

It may reasonably be concluded that circumstantial evidence implicates polyphenols from fresh growing leaves in the movement of iron in soil profiles. A similar mechanism is not impossible for aluminium. The evidence given here and by other authors (cf. Bloomfield, 1957) shows that polyphenols are present, have the potentialities required for the task, and, with low base status soils, favourable conditions for action.

Acknowledgements

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THE MECHANISM OF SURFACE NITRATE ACCUMULATION ON A BARE FALLOW SOIL IN UGANDA

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Summary

In a red latosol loam under bare fallow at Kawanda, Uganda, nitrate accumulates to as much as 70 p.p.m. nitrate nitrogen during short periods of dry weather. Nitrate accumulation appears to be a microbiological process involving nitrifying bacteria similar to *Nitrosomonas* and *Nitrobacter*. Nitrate accumulation in an isolated topsoil, 3 in. deep, ceased when the moisture content fell below 10 per cent. Accumulation continued on plots which were in contact with the subsoil and which remained at 10 per cent. moisture.

It was concluded that under the conditions of these experiments, transport of ions to the surface by capillary transport or diffusion does occur, but is not responsible for the major nitrate accumulation, which seems to depend on progressive drying of the topsoil during which nitrate, as formed, becomes protected by the dry conditions from microbial reduction, assimilation, and leaching. Any process which prevents the progressive drying, e.g. shading, mulching, and watering, can be expected to favour nitrate removal and so to prevent nitrate accumulation.

Introduction

A NUMBER of studies have been made in the last 30 years of the seasonal variations in available-nitrogen status in different tropical soils. The results show that the nitrate status of the topsoil fluctuates considerably, thus varying the supply of available nitrogen to annual crops. Ammonia may accumulate under dry conditions (Robinson, 1957) but the variations in nitrate concentration are generally far greater than those in ammonia concentration and thus are more important to the crop.

Very different patterns of nitrate fluctuations have been obtained under different soil and climatic conditions. Nitrate may accumulate in the topsoil during the dry season, or the nitrate status may remain low (Hagenzieker, 1957; Greenland, 1958; Hardy, 1946; Leutenegger, 1956). A flush of nitrate may or may not be detected in the topsoil at the start of the rains (Birch and Friend, 1956; Birch, 1958). The factors which determine the pattern of accumulation in different ecological zones are not at all clear, but the following are probably important.

(*a*) The extent of the dry periods and the intensity of drying after each wet period—as controlled by temperature and humidity.

(*b*) The pattern of rainfall at the onset and close of the rains, which may determine the extent of nitrate accumulation before leaching or redrying prevents further accumulation.

(*c*) The soil type, with particular reference to the total nitrogen status, the texture and structure of the topsoil, and the status of other nutrients essential for bacterial nitrification.

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The present study was undertaken to examine the mechanism by which nitrate accumulates in the soil at Kawanda, near Kampala, Uganda, described by ap Griffith (1951), i.e. a red medium loam latosol of 0·15 per cent. total nitrogen and pH 5·8–6·0 under a bimodal rainfall averaging 43 in. per annum, and under a bare, weeded fallow.

Several tentative explanations have been put forward on the mechanism of nitrate accumulation in this soil. Meiklejohn (1953), on examining Kawanda soil, found bacteria of the classical *Nitrosomonas* and *Nitrobacter* types. ap Griffith (1951) had previously shown that nitrate accumulated to a high level on bare fallow soil, but that the accumulation was greatly suppressed in the presence of shade or mulch. Meiklejohn suggested that the important criterion might be the balance of nitrification and nitrate reduction or assimilation in the field, rather than the absolute population of nitrifying bacteria. The field data could easily be explained if the nitrifying bacteria were more active under drier conditions than the denitrifiers and nitrate-assimilating bacteria which are also present in this soil.

Workers in south-eastern France, Drouineau, le Fevre, and Blanc-Aicard (1953), found that mineral nitrogen was produced in dry soil at less than 6 per cent. moisture both in the field and in the laboratory. Their explanation was a non-biological decomposition of organic matter under dry conditions. Birch (1958) and Greenland (1958) have both given evidence for a release of readily nitrifiable organic nitrogen during drying, which results in a rapid production of nitrate on remoistening the soil.

Crowther (1952) put forward a further hypothesis for the mechanism of nitrate accumulation at Kawanda under dry conditions. He suggested that the surface accumulation of nitrate may be due not simply to nitrification in the topsoil, but also to a capillary movement towards the soil surface of nitrate which had been leached to the subsoil during the previous rains. Crowther visualized an upward transfer of nitrate in the soil solution, followed by evaporation and deposition of nitrate at the soil surface. Mills's (1953) results showed that the major accumulation of nitrate on bare-fallow plots, which were allowed to 'cap' with a surface crust for ease of sampling, was in the surface inch of soil. This result was in direct agreement with Crowther's hypothesis.

Each of these different explanations of the mechanism of nitrate accumulation at Kawanda has been critically examined in experiments designed to determine the importance of the suggested mechanism.

Analytical and Experimental Techniques

Field techniques

Six field experiments were done at the Kawanda Research Station: one on an area with an initial topsoil reaction of pH 5·0, and the rest on a site of good fertility, total nitrogen 0·17 per cent., average reaction pH 6, total exchangable bases 10–11 m.e. per cent., Truog extractable phosphate variable but mainly high (50–100 p.p.m. P_2O_5). All the experiments were laid out in randomized blocks or Latin Square designs; three on plots of 12–16 sq. yds., the other three on micro-plots of

1 sq. yd., enclosed by a wooden frame surrounding each plot from 3 in. above the soil surface to 6 in. below. There were either four or six replicate plots for each treatment. Chemicals were applied mainly in solution as sprays.

Soil samples were taken with 1-in. split-tube augers, six cores per plot being bulked, and sub-samples of 25 g. taken for nitrate determinations. Coefficients of variation of 20–25 per cent. were usual in the nitrate results, of which 7–10 per cent. occurred in the laboratory as errors of sub-sampling, extraction, and colorimetric measurements.

Laboratory techniques

Nitrate was extracted from the sub-samples by the method of Harper (1924), and estimated with brucine after Snell and Snell (1953). Chloride was estimated on the extract with silver nitrate (Snell and Snell, 1953). Nitrite was not determined on field samples, as the amounts were known to be very small.

Incubation experiments in the laboratory were usually done with 30-g. samples of fresh soil in sealed bottles at 35° C. The bottles were aerated daily for 5 min. Enrichment cultures, in the *Nitrosomonas* medium of Lees (1952) inoculated with 0·5 g. fresh soil, were used as a rapid test for the presence of nitrifying organisms. Nitrite was estimated in these, and in the incubated soil samples, with improved Griess–Ilosvay reagent after Snell and Snell (1953).

Results and Discussion

1. *The importance of microbiological nitrification during nitrate accumulation in the field*

Mieklejohn (1953) first reported the presence in Kawanda soil of nitrifying bacteria agreeing morphologically with, and showing reactions according to, the established characteristics of *Nitrosomonas* and *Nitrobacter*. Recent studies with enrichment cultures have shown the presence of ammonia-oxidizing organisms in soils from all districts of the Protectorate. Nitrifying organisms were present in all the major soil types from sands to heavy clays. The only cases where nitrifiers were not found on examination were an extremely acid (pH 3·0) oxidized swamp soil from Kigezi and a heavy sodium-rich clay from the Semliki Valley.

Estimations of the number of *Nitrosomonas* in several soils examined at Kawanda by Millbank (1956) indicated a high number of ammonia-oxidizing organisms, 20,000 per g. fresh soil, in Kawanda soil which was newly opened from a thick cover of Elephant grass (*Pennisetum purpureum*). Soils from five Northern Province variety trial centres, varying from sandy loams to a red clay loam, contained much smaller numbers of ammonia-oxidizers all within the range 1,800–2,300 per g. fresh soil. In each case the organisms produced nitrite according to the classical reaction of *Nitrosomonas*.

Enrichment cultures of the nitrifying organisms were prepared by inoculating culture media suitable for *Nitrosomonas* and *Nitrobacter* with samples of Kawanda soil. Active cultures were obtained of both

ammonia and nitrite oxidizers, and sub-cultures were made into separate media containing *d, l*-histidine, *d, l*-methionine, allyl thiourea, sodium cyanide, sodium fluoride, and sodium chlorate respectively.

The ammonia-oxidizing cultures were powerfully inhibited by allyl thiourea and less powerfully by histidine and methionine (all inhibitors at 0·002 M). The nitrite-oxidizing cultures were powerfully inhibited by chlorate and little affected by the other substances. These results are in agreement with the established effects of inhibitors on *Nitrosomonas* and *Nitrobacter* in temperate regions (Quastel and Scholefield, 1951; Hofman and Lees, 1953; Lees and Simpson, 1957). There can be little

TABLE 1

The Effect of Sodium Trichloracetate on Nitrate Accumulation in Bare Soil

Nitrate as p.p.m. NO_3-N in the dry soil

	No. of days after spraying						
	1	*8*	*15*	*18*	*22*	*25*	*29*
Nitrate on sprayed plots . .	49·5	32·5	7·7	10·6	13·7	15·7	16·8
Nitrate on control plots . .	46·9	40·1	8·8	17·4	36·9	34·3	39·4

Between day 15 and day 29 30·6 p.p.m. NO_3-N accumulated on the control plots but only 9·1 p.p.m. accumulated on the trichloracetate-sprayed plots. The differences were significant at $P = 0{\cdot}01$ on days 25 and 29.

doubt, therefore, that the classical nitrifying organisms are abundant in Kawanda soil.

A preliminary assessment of the importance of microbial nitrification in the accumulation of nitrate under field conditions was made by spraying bare fallow plots with a solution of sodium trichloracetate (TCA), as a general biological inhibitor. A heavy application (1,500 lb./acre) of TCA was used to provide about a 0·05 M solution of the inhibitor in the soil solution through the sampling region. The effect of TCA relative to the control plots began to show after rain had occurred 14 days after spraying, as a suppression of the nitrate accumulation as shown in Table 1.

A further experiment was conducted in order to examine the effects of soil reaction on nitrate accumulation under bare fallow conditions. The site chosen had an initial reaction of pH 4·9 and the treatments imposed were:

1. Untreated control, pH 4·9.
2. Sprayed with sulphuric acid to obtain pH 4·1.
3. Lime as calcium carbonate at 10 tons/acre to obtain pH 6·7.

Fig. 1 shows the effect of each treatment on subsequent nitrate concentrations in the 0–6 region.

The more rapid nitrification at pH 6·7 is evident in higher peak accumulations of nitrate, but a more rapid removal of nitrate after rain also occurs in this treatment, eventually causing the nitrate concentration to fall back to the control level. The differences due to this treatment

were significant ($P = 0{\cdot}01$) at the peak accumulations of nitrate, but the significance was lost after the rain towards the end of the sampling period. Both the peak nitrate accumulations and the range of fluctuation at pH 4·1 were considerably less than the control.

These results are entirely consistent with the operation of a microbiological nitrate-producing mechanism with an optimum at or near pH 7. The effects of ammonium sulphate and green manures upon nitrate accumulation (ap Griffith, 1951; Simpson, 1960) also indicate a vigorous microbiological nitrate formation. It appears likely, therefore, that the normal process of microbiological nitrification is *primarily* important in the production of surface nitrate accumulations. It is quite possible, however, that the high nitrate concentrations are produced not by microbiological nitrification alone but by a physical movement of nitrate, or a chemical release of rapidly nitrifiable organic nitrogen during drying which proceeds simultaneously with and augments the microbiological reaction. This possibility has been examined in the experiments described below.

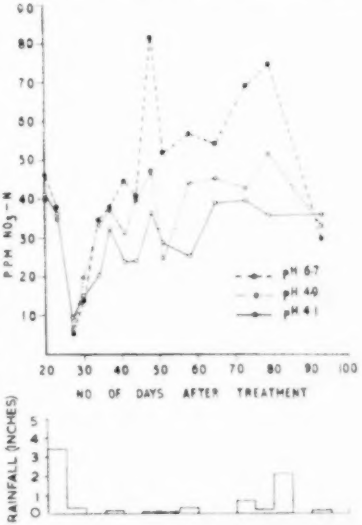

FIG. 1. The effect of soil reaction on the rate of nitrate accumulation under field conditions in bare fallow soil.

2. *Nitrate accumulation in the isolated topsoil*

A 'sheeted-plot' experiment was conducted at Kawanda in which nitrate accumulation was compared on bare control plots and plots in which the topsoil was isolated by a horizontal galvanized metal sheet, 3 in. below the surface. It was hoped that in this way the influence of moisture and nitrate in the subsoil on the surface nitrate accumulation could be followed. Each micro-plot was 1 sq. yd. in area and all plots, sheeted and controls, were similarly cultivated at the start of the experiment. Six randomized pairs of micro-plots were constructed and were irrigated once to aid consolidation before the initial sampling.

The surface of all plots was kept clean by hand-weeding with minimum disturbance while samples were being taken periodically in the 0–3-in. layer. During the first 2 months of the experiment, December and January, abnormally heavy rain occurred and the nitrate concentrations remained small, but during February and March drying conditions prevailed and nitrate accumulated. Fig. 2 shows the nitrate concentrations and moisture contents on the controls and sheeted plots during this period.

Nitrate accumulated on all plots as the moisture contents fell into the

10–15 per cent. range, the accumulation progressing rather more rapidly on the control plots than on the sheeted plots which were isolated from the subsoil. The sheeted plots then began to dry out more rapidly than the controls and nitrate accumulation stopped as the moisture content fell below 10 per cent. The control plots maintained a moisture content of about 10 per cent. and continued to accumulate nitrate.

Thus the main nitrate production appeared to be a biological process, inhibited by drought conditions at less than 8–10 per cent. moisture. There was no actual release of nitrate on drying which might be attributable to a non-biological release as found by Drouineau *et al.* (1953*b*). It was later shown (Fig. 5), using incubated samples in the laboratory, that nitrate formation does not occur in Kawanda soil when the moisture content is below approximately 8 per cent. In the above field experiment a substantial amount of nitrate, 34 p.p.m. NO_3–N, accumulated in the isolated topsoil while 44 p.p.m. NO_3–N accumulated in the control plots. This difference might be due to nitrate transported from below 3 in. deep—a possibility which was therefore examined.

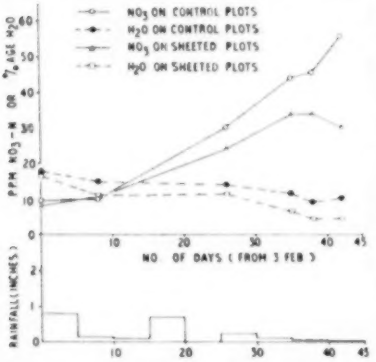
NO3 ON CONTROL PLOTS
H2O ON CONTROL PLOTS
NO3 ON SHEETED PLOTS
H2O ON SHEETED PLOTS
PPM NO3-N OR % AGI H2O
NO OF DAYS (FROM 3 FEB)
RAINFALL (INCHES)

FIG. 2. Nitrate accumulation under drying field conditions in bare topsoil (0–3 in.) when in contact with, and when isolated from, the subsoil.

3. *The movement of nitrate towards the soil surface*

A further experiment was conducted to assess the amount of upward movement of nitrate during a dry period, according to Crowther's theory. Three different techniques were involved in this experiment, known as the 'nitrate-inhibitor' experiment.

1. Two levels of original nitrate were imposed, namely the control level (N_0) and an application of sodium nitrate at 265 lb. N/acre (N_1). This applied nitrate was allowed to leach into the topsoil and adjacent subsoil during heavy rain, and the subsequent accumulation of nitrate in the 0–3-in. surface region was compared on N_0 and N_1 plots.

2. A basal dressing of potassium chloride equal to 600 lb. Cl/acre was applied to all plots so that salt movement within the surface regions could be determined by chloride analysis, without any interference from nitrification.

3. Two inhibitors, sodium cyanide and sodium chlorate, were applied as separate treatments with the object of disturbing the microbial activity in the topsoil, so allowing an assessment of the importance of such activity in the net nitrate accumulation.

The experiment thus had a 2 by 3 factorial design involving the two levels of nitrate and three inhibitor treatments, including control. The treatments were applied on 1 and 2 May assuming that the May rains would allow moderate leaching of the applied nitrate and chloride. In

actual fact the rainfall during May was heavy (9·42 in. beginning 2 May), but nitrate movement in this open-structured latosol loam was not as great as expected. On 22 May (= day 20), after 8·74 in. of rain, the greatest concentration of nitrate was still only 3–12 in. below the surface with a gradual decrease in concentration at increasing depths. At this time a mean concentration of 46·5 p.p.m. NO_3–N was found in the

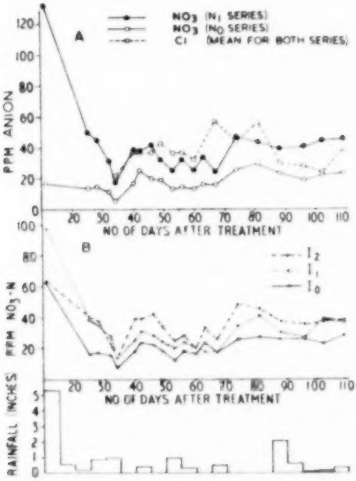

FIG. 3. Nitrate concentrations in the 0–3-in. surface layer during the nitrate-inhibitor experiment. A, The effect of applied nitrate (N_1) compared with the control (N_0). The broken line shows the level of chloride on the same scale. The difference between nitrate levels on N_0 and N_1 plots was significant ($P = 0{\cdot}05$) at each date throughout the sampling period. B. The comparative effects of the two inhibitors, cyanide (I_2) and chlorate (I_1), in relation to the control (I_0). The difference between nitrate levels on I_2 and I_0 plots was significant ($P = 0{\cdot}05$) for dates throughout each of the high nitrate periods—days 40–49 and days 74–102.

3–12 in. layer on the N_1 plots, and 10·0 p.p.m. on the N_0 plots. Leaching of the surface horizons continued until 5 June (day 34) when the 0–3-in. layers contained 17·6 p.p.m. NO_3–N on the N_1 and 5·6 p.p.m. on the N_0 plots. The difference between nitrate concentrations in the N_1 and N_0 plots on day 34 is presumed to be due to incomplete leaching.

Drying conditions began in June and continued through July and August (3·07 in., 3·11 in., and 0·95 in. rainfall respectively). Fig. 3 A shows the fluctuations in nitrate concentration on the N_0 and N_1 plots during this period. (Note first point on the graph is day 11; the very high figures in N_1 treatment before day 11 are irrelevant.)

During the whole experiment samples were taken from the 0–3-in. and 3–9-in. layers and the plots were kept free from weeds with the minimum disturbance. As drying began, nitrate accumulated in the 0–3-in. region on N_0 and N_1 plots at similar rates, and the fluctuations in nitrate remained reasonably parallel on the two treatments. The N_1 plots did, however, maintain a level of nitrate 10–20 p.p.m. N higher than the N_0 level, after the initial leaching had ceased. The mean nitrate values for this period (day 25 onwards) were N_0, 18·8 p.p.m.; N_1, 37·5 p.p.m.

Chloride figures were used only as an indication of the amount of salt movement towards the surface. On day 34, after the main leaching had ended, a minimum value of 22 p.p.m. Cl was obtained for the 0–3-in. layer and this gradually increased to 56 p.p.m. on day 81. Then with the heavy rain on day 86, the chloride level dropped to 28 p.p.m. and remained low until the last week of the experiment when the concentration rose again to 44 p.p.m. Cl.

Two points arise from the chloride figures. First, salt movement towards the surface occurred between day 34 and day 81, giving an increase of 34 p.p.m. Cl in the 0–3-in. layer. Secondly, the low chloride figures in the second half of the sampling period indicate that the nitrate figures remained high after the rain on day 86, not because of upward movement, but because of some type of nitrate release which compensated for losses due to leaching.

The general conclusion from this experiment must therefore be that a limited upward movement of ions did occur, as proved by the chloride figures, but this movement did not produce any remarkably greater nitrate concentration on the surface of the N_1 plots where nitrate was available for upward transfer. However, deep samples every 6 in. to 6 ft., at the end of the sampling period, showed that 48 p.p.m. NO_3–N remained in the 0–6-in. layer on the N_1 plots with a gradual decrease to 8 p.p.m. at 66–72 in. deep. There must have been a considerable retention of nitrate in the upper horizons during the May leaching, or else a return to the surface of leached ions. The chloride figures for the 0–3-in. and 3–9-in. layers proved that a net gain of 16 p.p.m. Cl in the total 0–9-in. layer occurred between day 60 and day 81, due to upward salt movement from below 9 in.

The inhibitor treatments which were also imposed on this experiment are interesting from a different point of view and are better discussed in the next section.

4. *Nitrate reduction under wet conditions*

The above experiment demonstrated that large amounts of nitrate are not easily leached from the surface layers, but yet pronounced falls in nitrate concentration do occur after rainstorms of about 0·5 in., when the 0–3-in. layer may lose 20–30 p.p.m. NO_3–N within a week. Previous workers have attributed the loss of nitrate to microbial absorption or more commonly denitrification (Greenland, 1958). Meiklejohn (1953) reported the presence of denitrifying bacteria in Kawanda soil which, together with the probable high population of actinomycetes and

heterotrophic bacteria, could account for a rapid removal of nitrate in a moist soil.

In the laboratory, starting with air-dry Kawanda topsoil and moistening to 25 per cent. moisture (just below field capacity) with a nitrate solution adjusted to provide 100 p.p.m. NO_3–N on a dry soil basis, it was found that active nitrate reduction occurred. The transient formation of nitrite occurred in concentrations of up to 15 p.p.m. NO_2–N_1 during a 24 hours incubation. During 3 days the nitrate concentration fell to 55 p.p.m. NO_3–N. The formation of nitrite was powerfully inhibited by 0·002 M chlorate.

In the field, evidence for the operation of nitrate-removing microbiological reactions was obtained in the 'nitrate-inhibitor' experiment by applying sodium cyanide and sodium chlorate and following the effects of these inhibitors on the nitrate accumulation. The inhibitors were sprayed in solution on to bare fallow plots immediately after the nitrate applications had been made. The treatments were:

I_0 = No inhibitor control.
I_1 = Sodium chlorate (175 lb./acre).
I_2 = Sodium cyanide (400 lb./acre).

The inhibitors were leached into the topsoil by very heavy rain (cf. Fig. 3), run-off from the plots being prevented by box-bunding. After

TABLE 2

The Effects of Microbiological Inhibitors on Topsoil Nitrate Accumulation

Nitrate is given as p.p.m. NO_3–N in the 0–3-in. layer. Sampling was continued from 27 May to 26 August 1957, and the figures are means for twenty sampling dates.

	I_0 (*control*)	I_1 (*sodium chlorate*)	I_2 (*sodium cyanide*)	*Mean*
N_0 . .	13·5	18·4	24·5	18·8
N_1 . .	28·4	39·6	44·6	37·5
Mean .	20·9	29·0	34·5	28·1

On analysis of the inhibitor and applied nitrate factorial effects, the difference due to I_1 and I_2 versus I_0 was significant ($P = 0{\cdot}05$) at all sampling dates during the periods between days 40–49 and days 74–102. The $N \times I$ interaction was not significant.

There is a possibility that nitrate may eventually be formed from the decomposition products of HCN, arising from the action of *Thiobacillus* spp. followed by nitrification, which may account for the high N_0I_2 figure.

leaching, 22 p.p.m. Cl was found remaining from the sodium-chloride treatment which was also used in the experiment. If chlorate ions equivalent to 22 p.p.m. Cl also remained, from the chlorate treatment, a 0·003 M solution would be formed at 20 per cent. moisture. A solution of this order of concentration would be sufficient to inhibit nitrate reduction to a marked degree; and would remain effective for a considerable time as decomposition is slow (Quastel and Scholefield, 1951). No estimate can, however, be given for the time taken by the cyanide to decompose on the sodium cyanide plots.

Fig. 3B shows the nitrate fluctuations in the 0–3-in. region, as the means of the N_0 and N_1 levels of applied nitrate, for each of the inhibitor treatments. The nitrate concentration in treatment I_2 remained uniformly the highest, followed by I_1, and the control plots had generally the lowest nitrate values. Table 2 gives the mean nitrate concentrations for each treatment over the sampling period of 3 months.

Thus both inhibitors had a positive effect in maintaining a higher overall nitrate level. A possible explanation of this effect is that each inhibitor effectively decreased the amount of nitrate removal during each period of wet conditions. An alternative explanation of the effect of cyanide is that increased alkalinity affected the rate of nitrate formation.

A second experiment was performed with the object of assessing the amount of nitrate removal which can be caused by frequent moistening of the topsoil by rain in amounts insufficient to cause leaching through the 0–3-in. layer. The experiment involved three moistening treatments:

W_0 = Dry control.
W_1 = 0·1 in. of water applied twice weekly.
W_2 = 0·2 in. of water applied twice weekly.

TABLE 3

The Effect of Continual Moistening on the Nitrate Status of Bare Fallow Soil

Nitrate is expressed as p.p.m. NO_3–N in the dry soil for the 0–3-in. layer.

Date	W_0	W_1	W_2
16 January 1958	43·9	46·1	45·2
20 January 1958	43·4	39·6	34·9
23 January 1958	52·4	43·6	40·3
27 January 1958	69·3	58·5	53·2

On 27 January the effect of W_1 and W_2 versus W_0 was significant ($P = 0{\cdot}05$). There was no significant difference between the W_1 and W_2 effects, and practically no interaction of W (watering) effect with N (applied nitrate) effect. The reduction in NO_3 concentration ($W_1 + W_2$ versus W_0) was significant at $P = 0{\cdot}01$ on 23 January. There was no significant difference between W_1 and W_2. On 20 January the watering effect was not significant at $P = 0{\cdot}05$. This is considered to be very important evidence for the existence of nitrate removal on remoistening in the field.

These treatments were imposed on micro-plots of bare soil, each of 1 sq. yd., after basal irrigation with 0·5 in. of water had been given to all plots. The plots were sampled twice weekly in the 0–3-in. layer before each watering, and it was found that practically all of the applied water was lost by evaporation between applications. Plastic covers were used on the plots overnight and to avoid moistening by sudden storms during the day, but the covers were removed for as long as possible during daylight hours. The covers, which were made of Visqueen plastic film, were fitted to leave several inches of air-space above the soil surface while in use. The experiment lasted for one month (January) during the driest part of the year.

Nitrate accumulation after the initial moistening on 20 December was rather slow on all plots, possibly because of the undisturbed, compact condition of the topsoil, but an increase in nitrate took place during 13–16 January with no appreciable differences between treatments. Then in the interval 16–20 January the moistened treatments (W_1 and W_2) both showed a loss of nitrate and remained lower than the W_0 controls until the close of the experiment as shown in Table 3.

5. *The suppression of nitrate accumulation by shade and mulch*

The effect of mulch in suppressing the nitrate accumulation at Kawanda was originally described by ap Griffith and Manning (1949). ap Griffith (1951) then showed that both mulch and shade produce this suppression. The effect of mulch on the soil nitrate level might be attributed to several factors, namely decreased temperature, increased moisture content, decreased aeration, and also microbial absorption of nitrate when organic matter with a high carbon-nitrogen ratio is added. Shade produces effects similar to mulching except that the carbon-nitrogen of the topsoil is unchanged. The effects of mulch and shade upon nitrate concentration have been critically compared in a micro-plot experiment.

The treatments were:

1. Bare fallow, clean weeded and cultivated on the surface with a small hoe.
2. A shade of Elephant grass reeds strapped together, resting on the soil surface. This was removed to allow cultivation as in (1).
3. A similar shade fixed 1 ft. above the soil surface.
4. A 2–3-in. mulch of *Imperata*. Not removed for cultivation. Sampling under the mulch was done with the minimum disturbance.

These treatments were replicated four times in a 4 by 4 Latin Square design. The site had a reaction of pH 6·0 and available phosphate was high (*c.* 150 p.p.m. Truog-extractable P_2O_5). Run-off from the plots was prevented by the surrounding frames. Fig. 4 shows the fluctuations in nitrate status on this site during the 3 months of sampling.

Sampling was started in the moist soil only one week after the treatments were applied; this accounts for the initial differences. Artificial moistening was then used, causing the high nitrate of the dry soil to be lost rapidly at different rates for the bare and shaded plots. Very significant differences between the bare and the shade and mulch treatments soon showed in the nitrate concentrations of 0–3-in. samples, and continued until the onset of heavy rains in April. A study of Fig. 4 shows that the mulch treatment (4) produced very similar nitrate values to the low shade treatment (2) in which incorporation of organic matter was prevented by inverting the shade after each sampling. Thus the suppression of nitrate accumulation by mulch does not appear to be associated with a modification of the carbon:nitrogen ratio of the topsoil. The raised shade treatment (3) showed a nitrate concentration intermediate between the values for bare soil and low shade but the difference

between the two shade treatments (2 and 3) became progressively smaller during the first 6 weeks of the sampling period and then ceased.

This result shows that there is no real difference between the action of shade and mulch, and also that the effect of shade becomes more marked as it is placed nearer to the soil surface. The effect of shade upon soil conditions is to decrease the temperature and hence the evaporation from the surface. The fact that a shade 1 ft. above the surface has rather

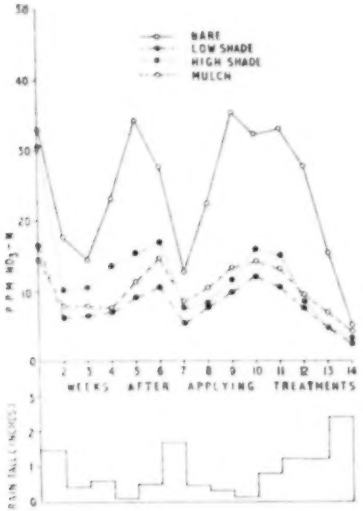

FIG. 4. The effects of shade and mulch on nitrate accumulation on fallow soil. The differences between bare and other treatments were highly significant throughout the peak accumulation periods. The differences between high shade and low shade were significant ($P = 0{\cdot}05$) for dates between 3 weeks and 6 weeks after applying treatments, but were not significant during the second accumulation—7–14 weeks. The differences between mulch and low shade treatments did not attain significance ($P = 0{\cdot}05$).

less effect than a shade on the surface suggests that the rate of evaporation, not the temperature which would be the same under high and low shades, is the important criterion. Since cover was complete in both treatments any slight difference in temperature would be due to varying insulation and not shade.

A subsequent laboratory experiment was performed in which small (30 g.) well-aerated samples of Kawanda topsoil were incubated for 2 weeks at 35° C. at a range of constant moisture contents, and the nitrate production at each moisture content was determined. Fig. 5 shows the results obtained.

Since the soil was air-dry before initial moistening, 'flush' nitrate may have been formed. The graph shows that nitrate accumulation increases with increasing moisture contents up to over 20 per cent. (compare Calder, 1957). Thus the suppressive action of mulch and shade on nitrate accumulation cannot be due simply to an imposition of higher moisture content at any one time, but rather to preclusion of the drying cycle which normally alternates with a wetting cycle on a bare fallow soil in the field.

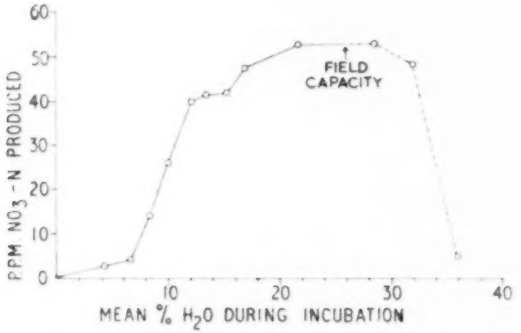

FIG. 5. The relationship between nitrate accumulation and moisture content in well-aerated, incubated samples of Kawanda topsoil. The dotted part of the curve represents moisture contents greater than field capacity.

Conclusions

Four processes have been shown to influence the accumulation of nitrate in the bare topsoil at Kawanda.

1. Bacterial nitrification, which occurs very rapidly under gradual drying conditions.
2. Movement of nitrate ions by diffusion or capillary transport from several inches below the surface to the 0–3-in. region. The conditions under which this attains importance are probably very limited.
3. The microbiological removal of accumulated nitrate on remoistening after a dry period. The evidence for the existence of this process occurring in the field is somewhat circumstantial and cannot yet be regarded as conclusive.
4. Leaching during heavy rainstorms.

Each of these processes has been found to occur to some extent under field conditions but the importance of each at any one time is controlled by moisture and temperature conditions. Nitrification is very important in the accumulation and can continue in the topsoil until the moisture content falls to 8 per cent.

In the 'nitrate-inhibitor' experiment there was a distinct tendency for nitrate and chloride ions to remain in the 0–3-in. and 3–9-in. surface

horizons, but movement upwards from the 3–9-in. to the 0–3-in. layer amounted to only 30 p.p.m. in the 0–3-in. layer over 3 months. However, it would be unwise to generalize on the results of this experiment and possibly, under more favourable climatic conditions, greater movement can be obtained.

The rapid removal of accumulated nitrate on remoistening has been demonstrated in the laboratory and, if the effects of chlorate and cyanide as inhibitors can be accepted as evidence, there is a rapid decrease in nitrate level due to microbiological removal of nitrate in the field. This conclusion is supported by the effects of frequent watering on nitrate level in the field. Again, when the topsoil moisture was conserved by mulching or shading, suppression of nitrate accumulation was observed, which did not occur at high moisture contents in well-aerated samples in the laboratory.

These points of evidence all suggest that nitrate accumulation in the field depends upon a progressive drying period after rain, in which the topsoil is gradually drying to an increasing depth. Under these conditions, aeration and soil temperature are favourable for rapid bacterial nitrification and also encourage the retention of nitrate ions in the surface. As long as the drying cycle continues and the moisture content remains above 8 per cent., nitrate will accumulate and remain 'fixed' in the dry topsoil. The sudden entry of rain into this warm, dry topsoil, rich in nitrate, produces reducing conditions and nitrate is removed biologically as well as physically by leaching.

No evidence has been found for a sudden flush of nitrate on remoistening the dry soil, as reported by Birch (1958), Hagenzieker (1957), and Greenland (1958). Any release of nitrifiable nitrogen during drying followed by rapid nitrification on remoistening is probably masked, if it does occur, by the reduction of nitrate which has accumulated within the drying period before moistening. Thus it appears that the drying period is the essential period in nitrate accumulation and that the balance of nitrate formation and removal during drying strongly favours nitrate accumulation—to an extent which does not occur during incubation at a constant moisture content.

There has been no evidence to support the theory of Dhar *et al.* (1933) of photochemical nitrification. Incubated laboratory samples are capable of releasing as much nitrate during 3 weeks in the dark as can normally be found in the field. Similarly, nitrate accumulation in the dark stops at about 8 per cent. moisture, just as it does in the field.

On the other hand temperature might be fairly important during the dry season when the main nitrate accumulation occurs. One of the effects of shade and mulch is to reduce the soil surface temperature by about 4–5° C. (ap Griffith, 1951). Such a small change in temperature, however, is unlikely to have a pronounced effect on the rate of nitrification, according to the results of Hall (1924) in South Africa and Prescott and Piper (1930) in South Australia. At Kawanda it has been noted that during a long dry period when the moisture content under mulch approached that of the bare soil surface, the nitrate concentrations tended to equalize. Thus although temperature changes cannot be

entirely excluded as unimportant, they are unlikely to affect the general pattern of accumulation.

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THE BUTANA GRASS PATTERNS

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In a recent issue of this journal G. A. Worrall (1959) gave a thorough account of the grass patterns in the Butana, Sudan. He considered three possible modes of origin and concluded that none was entirely satisfactory: firstly as incipient gilgai following lateral mechanical eluviation; secondly as a result of rhythmic deposition of vegetable debris by gentle sheet flow; and thirdly as a result of soil cracking (soil creep) due to gravitational pull downslope. Serious objections to each of these hypotheses arise; lateral mechanical eluviation is unlikely to be effective through a moist soil with 20–35 per cent. montmorillonite; only small-scale lines of vegetable debris like ripple marks have been observed; and soil creep is not normally considered on slopes of 1 in 200 (18 min.). This note outlines an additional possible mode of origin acting in combination with gravitational pull downslope (cf. Worrall, p. 52).

After heavy rain a threefold moisture pattern is repeated parallel with the contours. The grass bands are relatively moist, the bare ground is dry, and between them are narrow cracked strips of soil saturated to a depth of about 50 cm. Considerable expansion occurs beneath the cracked strip and the grass band. Part of the volume increase will be taken up by the closure of cracks and cavities ('pot-holes' is not a good term), and part will be expended by a rise of the ground surface. However, a small residual force may act laterally and will be more effective downslope in the more plastic moist soil than upslope against the less plastic dry block. This may result in some compaction or upraising of the soil at the downslope margin of the grass band, and in a line of cracked soil with cavities at the upslope margin of it. Downslope movement into the cracked strip after heavy rain is effected by creep, slip, slump, expansion, and perhaps minor mechanical eluviation. Dr. Worrall's observations indicate that these cracked strips migrate upslope at about 1 m. every year and average about 30 m. apart. Therefore on the average every part of the slope is worked over every 30 years. A cracked strip forms before the pioneer grass (*Cymbopogon nervatus*) in upslope migration. Later cracked strips with cavities develop followed by a variety of grasses. This suggests that the cracked strips start the cycle of grass pattern migration. How, then, do the cracked strips form?

Wetting and drying of these heavy clay soils causes the formation of innumerable cracks some of which are orientated radially and concentrically on individual rises. Water is more likely to be retained in the concentric cracks than in the radial ones, and repeated saturation, expansion, and contraction will preferentially enlarge them. Larger

cracked zones may develop at the expense of smaller ones and extend laterally along the contours. The distance between them may well be a function of the slope as suggested by Worrall (p. 38). Concentration of water in the severely cracked strips would cause greater plasticity around them and the upslope soil would move into the cracks causing an annual migration upslope. A small gravitational pull will aid in this development. At some early stage in this process grass seeds washed down the larger cracks will have suitable moisture conditions for their growth (cf. Worrall, p. 52). A radial and concentric cracking pattern would also be favoured by the presence of an upper migratory layer derived from the upper slopes and diverging and thinning out on the side slopes of the gentle rises. In our opinion the lighter texture of the upper layer and the distribution of quartz fragments through it suggests this.

Mechanical eluviation is not considered an important process in this grass pattern formation. For active mechanical eluviation to occur there must be a considerable range in the grade size of the debris, a powerful flow of subsurface water, and available space into which the fine particles can move (Ruxton, 1958, p. 375). Such conditions are not present in nearly impermeable clay loams on slopes of 1 in 200. Lateral mechanical eluviation often occurs along a coarse-textured zone (stone layer) between the migratory layer and the sedentary weathered rock (Charter, 1949; Nye, 1954). But, on the Butana, the clay loams average about 3 m. in thickness usually with no stone layer even at the base (except along the wash courses). The cracked strips with cavities do provide free faces, but it seems that the bare patches upslope admit and retain the least moisture.

Worrall (p. 38) notes the absence of grass patterns on slopes of less than 1 in 400. We have noted that grass patterns, often of different type from that described by Worrall, are common on the degradational clay plains between the Blue Nile and the Atbara and are not recorded on the aggradational clay plains of the Blue Nile basin and the Gezira. The non-stratified clays of the degradational plains are from 1–6 m. thick (on weathered rock) forming slopes of 2–5 m. per km. and contain little salt. Those on the aggradational plains are stratified with a high salt content and are 3–30 m. thick. They form slopes of about 0·2 m. per km., and overlie 6–50 m. of arenaceous sediment.

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TREE PATTERNS IN THE SUDAN

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Summary

Bands of acacia trees rhythmically disposed occur in the Sudan in a form resembling grass patterns. They have been found only on the red sand belt of Western Sudan, and aerial and ground observations and measurements seem to indicate that they all lie on gentle slopes very roughly on the contour, that they are as much as 200 m. wide with similar or wider spaces between them usually occupied by ground patchily covered by grass.

Though sometimes tree bands may have a man-made origin, the cause is generally natural and is probably the same as that producing grass patterns.

TREE patterns occur in the Sudan in a form resembling the vegetation patterns described by MacFadyen (1950) and the grass patterns described by the writer (1959). They were referred to in the latter paper and subsequently further study of them was made by aerial and ground observations.

Aerial observations by the writer and Captain J. Landless of Sudan Airways indicated that the tree patterns occur sporadically in the semi-arid western Sudan on the extensive red sand formation known as the 'Goz'. This is in contrast with the grass patterns which occur on the semi-arid clay lands of the Butana in eastern Sudan. The difficulty of locating the patterns on the ground and, when this has been done, of surveying them with any certainty has not been properly overcome. In country where there are few landmarks it is obviously difficult to pin-point sites, and this becomes much more so in wooded country, but several sites were located on the ground, and one, near Khartoum, has been examined in some detail.

Aerial observations

From the air the patterns appear to be larger than the grass patterns (Plate I *a*, *b*). They are bands, usually curved and running in broken lines approximately parallel to each other, and with a spacing apparently several times greater than the bands themselves. They appear dark green or blackish from the air, and the intervening spaces red or red-brown. They may resemble tree-lined water-courses, but are distinguished from these by their regularity, parallel disposition, and discontinuity—they do not link up to form systems. Within an area there may be sets orientated in different directions, so that they are not dune forms developed by wind action. Where water-courses occur the patterns generally lie approximately at right angles to them, as though lying on the contour, with the convex side facing downslope as in the Butana grass patterns. In Kordofan and Darfur (western Sudan) they are usually associated with grass which forms a continuous band on one side of the tree bands (probably the downslope side), and passing outwards to grass patches which occupy the rest of the space between the

bands. Occasionally the bands appear to be wholly trees. In the area 40–70 miles north of Malakal, on the west side of the Nile, occur red patches, usually elongated, in an area of brown soil. On these, which are probably sand drifts, corrugated lines of trees occur which are orientated approximately at right angles to the length of the patch where there is any elongation. Where the patch changes direction the tree bands change also.

Estimation of the size of the Malakal patterns indicated that they are from a few trees to about a dozen trees wide: this would probably mean about 10–100 m. wide. Elsewhere they are sometimes greater than this—200 m. or more across.

Ground observations

1. At 15 miles east of Um Saiyala (approximately half-way between Khartoum and El Obeid). These were the first patterns to be located on the ground, and there was some uncertainty at the time as to where the real thing was being observed. Irregular belts of woodland alternate with open grassy ground containing a few scattered trees. The open ground is 200–400 m. wide, and the treed areas about half this, though it proved difficult to draw the line between the two. The trees were nearly all acacia, chiefly *A. mellifera* and *A. nubica*, together with some *Comphera* sp. The grass was patchy and chiefly *Aristida*, sp. On the open ground the soil was strewn with ironstone gravel, and it was compact and difficult to dig. In the treed areas the surface is irregular, and evidently remains wet and soft after rain as it was much cut up by tracks of vehicles.

2. At Jebel Mandara, 10 miles south of Jebel Aulia Dam, west bank of White Nile. This was first sited from the air and then pin-pointed from the top of Jebel Mandara (Plate II*a*). Even then it proved difficult to be certain of one's position in the bands because it was not possible to get a view far above the trees. A helicopter would be ideal for observation of these patterns, but in the absence of this, some help was gained by setting up a step ladder on the top of a land rover. The trees are nearly uniform in height (Plate II*b*) usually about 8 to 10 ft., and it is possible by this means to see over their tops to the next band.

Here the change from grass of the open ground to the tree band is sharp on the upslope side (Plate II*b*), irregular and indefinite on the downslope side. The open areas are patchily covered with grass, chiefly *Aristida* sp. and *Schoenfeldtia gracilis*, and the patches are often potholed as in the grass patterns of the Butana. In some places there appears to be a suggestion of banding in the grass. The bare ground is panned and gravel-strewn, the stones consisting of ironstone, quartz, and sandstone. The soil is sandy, dry, and compact. The grass becomes thicker and continuous at the forefront of the tree bands, but becomes thin and patchy again under the trees, and if the band is wide the grass may disappear entirely. The trees are fairly uniformly spaced at 3–7 m., though some thickets occur where the trees are small and close. They are an almost pure stand of *Acacia tortilis*.

Measurements of widths and levels (Table 1) using a dumpy level and

TABLE 1

Measurements of Tree Patterns at Jebel Mandara and Sheikh El Siddig

	Width		*Ratio*		*Level across band*				
	Treed (m.)	*Bare (m.)*	*Treed: bare*	*Level along band*	*Bare*	*Treed*	*Bare*	*Treed*	*Bare*
Jebel Mandara:									
Site 1	108	140	1 : 1·3	Slope 1 in 2,300; irreg.	Constant fall of 1 in 330	Irreg.: max. rise 0·29 m.	Constant fall of 1 in 160	Irreg.: max. rise 0·12 m.	..
	110	..				max. fall 0·06 m. from front		max. fall 0·05 m. from front	
Site 2	45	68	1 : 1·5	Slope 1 in 346; slightly irreg.	..	Irreg.: max. rise 0·03 m.	Constant fall of 1 in 205	Constant rise of 1 in 1,120	Constant fall of 1 in 450
	45	45	1 : 1			max. fall 0·04 m. from front			
Site 3	48	185	1 : 3·8	Slope 1 in 700; slightly irreg.	..	Irreg.	Constant fall of 1 in 810	..	..
Sheikh El Siddig:									
Site 1.	75	..	..	Slope 1 in 750; reg.	..	Constant fall of 1 in 240	Constant fall of 1 in 170	..	..

pacing were made along the front of the tree bands and at right angles to this across the bands. The first is fairly easy to do as there is usually little doubt where the front lies, but the second is more difficult as the trees thin out and do not end sharply on the downslope side. It will be seen from the measurements made that the widths of the tree bands lie between about 45 and 140 m., and if the uncertain figure of site 3 be ignored, the ratio of treed bands to bare intervening areas lies between 1 and 1·5 to 1), a closer ratio than appears from those patterns seen from the air.

The levels taken along the fronts of the tree bands show that they have a very gentle slope which is slightly irregular. They are thus not as close to the contour as the grass patterns. Measurements across the bands are rather inconsistent, but it may be tentatively stated that the slope is regular on the non-treed areas, but irregular and sometimes tending towards a rise under the treed areas. Direct observation often bears this out, the ground surface under the trees being irregular.

3. At Sheikh El Siddig, about 40 miles south of Jebel Aulia Dam. These show up well from the air, but on the ground appear rather irregular and difficult to measure, and it is often difficult to distinguish between true bands and tree-covered drainage lines. The banding or patchiness is often related to sequences of slightly raised belts of land which are covered with ironstone gravel, hard and generally bare of vegetation, and sandy edges which support the trees.

Measurements of one band at 5 miles north-west of Sheikh El Siddig are given in Table 1. These are similar to those of Jebel Mandara, except that under the trees the fall was fairly steady, and broken only by a ridge, evidently artificial, running longitudinally in the tree belt. It is possible that this band may have an artificial origin, the ridge being an old 'teras' which was made to impound the water during the rains and so provide better conditions for the growing of the millet sown afterwards. With the abandonment of the site the continued increased supply of water would favour tree growth and eventually a band would be produced.

Elsewhere in Kordofan the writer has sometimes observed that patches of trees forming a rough circle occur in otherwise open ground. It seems possible that these too could have a man-made origin, being old sites of *zeribas*, i.e. protective fences made of dead acacia thornbush laid side by side to enclose farm produce, animals, or buildings. These *zeribas* would collect drifted dust and sand, and together with the richer organic soil provided by animal droppings would encourage good vegetational growth. Once begun the trees would probably improve the soil conditions by trapping more loose material and moving surface water, and there would be a tendency for the patch to expand.

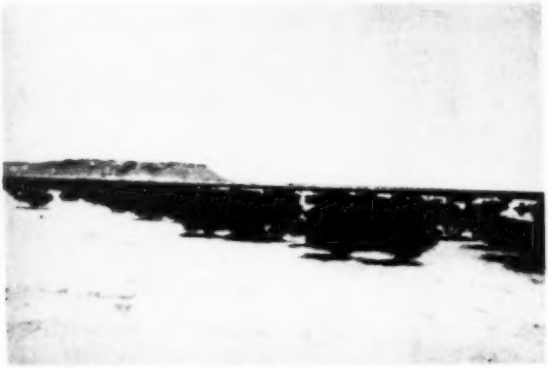
As yet there does not seem to be enough knowledge to explain the origin of the patterns. A suggested reason given for the origin of the grass patterns may apply to the tree patterns, i.e. that they are initiated on a surface which through the action of rain water has alternately panned surfaces and lines of loose, drifted material lying approximately on the contour. But as yet it is not certain that the tree bands lie very

a. About half-way between Khartoum and El Obeid. Aerial view of tree patterns

b. About half-way between Khartoum and El Obeid. Aerial view of tree patterns with wide tree-covered *wadi* in the centre

G. A. WORRALL—PLATE I

a. View of tree patterns from the top of Jebel Mandara
Foreground: scattered trees, cattle, and small tree-lined water courses
Middleground: sandy-bottomed tree-lined wadi
Distant ground: tree bands convex to the right (west)



b. View looking north to Jebel Mandara
A tree band, and just visible beyond, is the bare ground before the next band

G. A. WORRALL—PLATE II

close to the contour. The irregularity under the trees resembles that under the grass of the grass patterns, except that it is much greater under the trees and may result in an overall rise in the general direction of the downslope. This favours the second suggestion made for the origin of the grass patterns, that gravitational slip occurs in a rhythmic form, resembling 'sheep-tracks' on hillsides in temperate lands, but on a broader scale and on very gentle slopes.

The differences of vegetation and of soil between the tree patterns and the grass patterns do not necessarily indicate any fundamental difference in their origin. They both occur in semi-arid conditions, and it has been shown by Smith (1950) that in the Sudan sandy soils are more favourable to tree growth than are clay soils, climatic conditions being equal.

More work is needed on this problem before any certainty can be put to these hypotheses, and it is suggested that low-level aerial photography of chosen areas would be a desirable preliminary to surveys on the ground. Failing that, any device for lifting an observer even 10 m. off the ground would be a great advantage.

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POST-GLACIAL SEDIMENTS AS A RECORD OF REGIONAL SOIL DRIFTS

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Summary

Analytical data are given for deep-water sediments from Esthwaite Water in the English Lake District representing different depths below the mud surface and sediments of ages back to and including the late-glacial, of which the pollen status is known. Nitrogen content and loss on ignition increase steadily in muds laid down during the time of post-glacial forest development, showing also a small previous rise which represents the temporary late-glacial climatic amelioration (Allerød). Nitrogen remains approximately constant in muds representing the stage of post-glacial alder–oak–birch forest. Deforestation, as shown by increases in grass pollen in the muds, is associated with falls in the values for nitrogen and loss-on-ignition. These decreases occur in two stages, believed to represent two stages of human settlement and land use.

Analyses for elements such as sodium, potassium, magnesium, calcium, and iron, show signs of increasing solubility in the muds representing the time of forest development. Thereafter the amount of calcium diminishes progressively in later muds, while the Ca/Fe ratio falls, changes which could be correlated with the leaching effects of a rainfall of 170–200 cm. per annum on the soils in the lake basin. Similar data are recorded for a core from Rydal Water.

The results are interpreted as records of the regional changes in soils from the lake drainage systems during the post-glacial period.

INTEREST in the lake sediments of the English Lake District started in 1938–9 as a result of a bathymetrical survey of the lakes, using a Kelvin-Hughes echo-sounding apparatus. This gave records showing a series of echoes from below the bottom mud-surface. These echo-giving layers are evidently due to differences in density in the mud deposits and, in addition to those at obvious mud–rock interfaces, have been found to occur at the zone where glacial clays are replaced by post-glacial muds. Various diversities in sediments thus revealed have been used in following the late-glacial and post-glacial history of the district.

The characteristic late-glacial deposits are laminated clays—interrupted in suitable places by deposits often rich in littoral diatoms and with traces of a sub-arctic flora, Allerød in age, which precedes signs of a final mountain or corrie glaciation (Pennington, 1943, 1947). The post-glacial deposits are brown muds, usually about 4·5–5 m. in depth. The diatom and pollen series in these deposits have been worked out in Windermere by Pennington and in Esthwaite Water by Franks (1956). This paper deals with the chemical characters of four deep-water cores, three from Esthwaite Water and one from Rydal Water.

The general pattern of post-glacial change in the Southern Lake District is that there was a development of forest, through a mainly birch–pine phase to mixed alder–birch–oak forest, which started about 8,500 years ago and maintained itself little altered for some 4,000 years or more. Deforestation, shown by the spread of grass-sedge pollen and

the decrease in tree pollen, followed, apparently in two phases (cf. Franks, 1956), an early, milder one and a later and more complete with an intervening period of partial recovery. This is mentioned because parallel features occur in the chemical analyses. The two phases of deforestation agree in approximate time (based on the time scale for lake sediments) with the neolithic occupation of the district after about 1800 B.C. and the Norse clearances after A.D. 1000. There has been much amenity planting in the last two hundred years (cf. Pearsall and Pennington, 1947).

Material

The three main cores described here were taken from the deepest part of Esthwaite Water (about 13 m.) near the permanent 'centre buoy' maintained by the Freshwater Biological Association.

They show a characteristic appearance of about 4·6 m. of brown post-glacial mud overlying a greyer transitional region which merges into laminated clays below 5 m. The upper 2 m. (approximately) of mud shows a very slightly lighter colour which becomes more apparent especially in the topmost 70 cm. or so after the organic matter is oxidized by exposure to air. In the echo-sounding records faint traces of a change in mud density are often evident at a depth of about 40 per cent. of the brown mud. Broadly speaking, above this is the zone representing more or less clearly the period of progressive forest clearance. Faint silt bands are sometimes found in the mud.

Methods

The cores were taken with the modified Jenkin sampler (Jenkin *et al.*, 1941) used at that time, and some allowance has to be made for the possibility of slight errors in successive overlapping segments, as well as for any variations in mud depth and stratification that occur. These cores were then analysed chemically for total nitrogen and organic content estimated as loss on ignition as the muds are non-calcareous, and mineral matter as described below.

Cores 1 and 2. The nitrogen content was determined on small amounts with a semi-micro Kjeldahl method so that replicates could be taken at the same level in the core; three were normally prepared and two estimated, the third being used only if the duplicates disagreed by more than 2 per cent. of the estimated mean. This method allowed any apparent silt bands to be examined. Faint silt bands were more clearly apparent in core 1, and this was in technical respects perhaps rather better than core 2. Dr. Pennington took some samples for pollen analysis from core 1. After the samples for nitrogen estimations were complete, rather larger samples (+10 mg.) were taken for estimates of loss on ignition. These are therefore less sensitive to small changes in mud composition and more nearly average values at the depths indicated in cm. below the mud surface.

In investigating the mineral properties of the cores it was considered desirable to use methods of soil analysis at first rather than those of complete analysis.

Cores 3 and 4. Samples 5 cm. in length were taken for mineral analysis from the core every 20 cm., or on either side of an obvious stratigraphic boundary. They were halved longitudinally, dried to constant weight in an oven at 105° C., and powdered with a pestle and mortar. Duplicate nitrogen determinations were made on each half sample by the micro-Kjeldahl method, using a sodium-selenate catalyst, and distilling in a Markham still. The loss on ignition of each half sample was determined in a muffle furnace at approximately 550° C. The duplicate ash samples were then mixed for further analysis. The ash was taken into solution in dilute hydrochloric acid (Piper, 1950, p. 264) and the insoluble residue was weighed, after re-ignition.

Sodium and potassium were estimated with an EEL flame photometer. Iron was estimated using potassium thiocyanate and comparing the colours obtained against standard solutions in a Unicam spectrophotometer. Calcium and magnesium were estimated by titration with standard versenate solution, using murexide indicator for the calcium titration and eriochrome black for total hardness, magnesium being found by difference. For these titrations it was found necessary to remove iron and aluminium from solution by carefully controlled precipitation and filtration (Piper, 1950, p. 282). Nevertheless, the total hardness figures showed considerable variability and accordingly the magnesium figures may be unacceptable. Aluminium, also estimated by difference in this method, is therefore ignored. Standard additions of calcium could be estimated accurately.

Estimates of Nitrogen and Loss on Ignition

The results are given graphically in Figs. 1 (nitrogen) and 2 (loss on ignition) in relation to mud depth. Starting from the lowest inorganic clays, they show a rise in the general nitrogen and organic contents which reach the general high level by about 400 cm. The small rise preceding the main one represents the short late-glacial climatic amelioration (Allerød).

There are clearly three mud-depth zones where lower values of nitrogen may be expected, one about 300 cm. not very thick in core 2, a broader and definite one from 200 to 150 or 140 cm., and a still larger one from about 75 cm. upwards. Of these, the first usually shows also a faint silt band, the second is generally just visible as possessing a slightly higher colour after the core has been in the air for some time, while the broad uppermost zone is then distinctly lighter in colour than the rest of the core.

In general, the two cores agree well. Although the silt band at 390 cm. in core 1 was not evident in core 2, there was a lower nitrogen value at that level. The apparent silt band at 360 cm. in core 2 also corresponded with a low level in core 1. It will be noticed further that there was agreement between the two cores in the points at which the higher values in each segment occurred, viz *c.* 495, *c.* 345, 270, *c.* 210, *c.* 135 cm. The principal discrepancy occurs just below 200 cm. (in both nitrogen and organic content) where core 2 shows a more rapid fall than core 1. This may be due to an error in equating the segments of core 2.

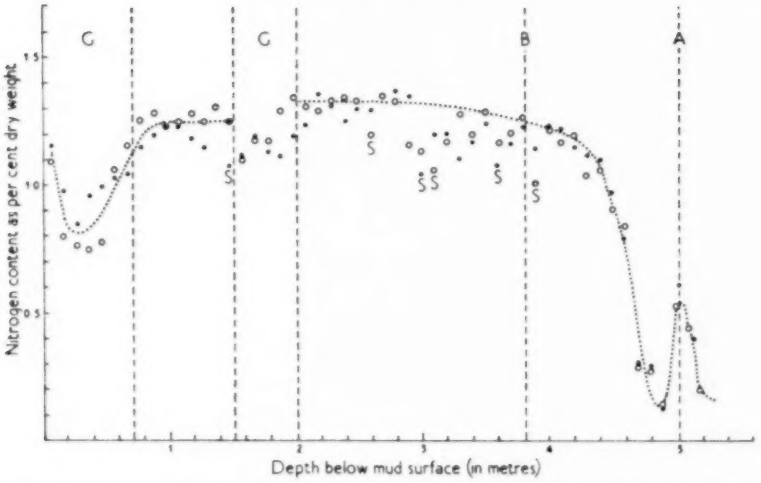

FIG. 1. Nitrogen content of bottom muds from cores 1 (circles) and 2 (dots) at different distances below the mud surface. G, zones of marked increase in grass-sedge and diminishing tree pollen; B, zone of establishment of alder–oak–birch forest; A, late-glacial phase of temporary climatic amelioration (Allerød); S, faint silt bands.

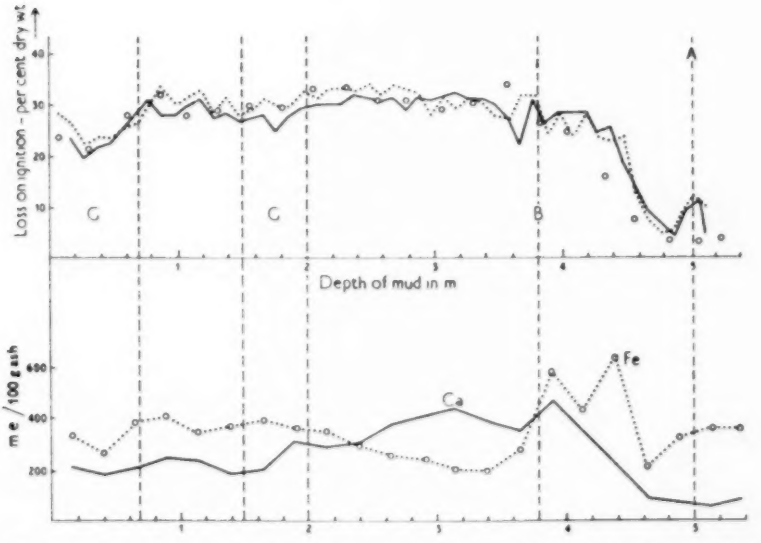

FIG. 2. *Above*: loss on ignition (as percent. of dry weight), 1 (continuous line), 2 (dotted line), and 3 (circles); letters as in Fig. 1. *Below*: iron and calcium × 20 content of muds from core 3 as m.e./100 g. of ash.

It is not argued that any single estimate in these data has high significance by itself. The general levels indicated by groups of results clearly have an appropriate statistical significance and the faint apparent silt bands, though of no great importance by weight in the general body of mud, clearly have lower than normal nitrogen content. On the other hand the zone from 200 to 275 cm. has a higher nitrogen content than the high level general elsewhere, e.g. 75–140 and 320–400 cm.

As the curve is drawn in Fig. 1 it indicates that the maximum nitrogen fixation in the muds is of the same order throughout the period of alder–oak–birch forest (380–200 cm.), but in the earlier part of this period the maximum level was often interrupted by conditions (e.g. inorganic silting) leading to lower nitrogen values.

These features are not so clearly shown in the data for organic content, which present more of the character of a smoothed curve, as would be expected from the method of sampling. The general features in the upper part of the core (200 cm. upwards) are similar to those given by total nitrogen—a fall in organic content above 200 cm., a recovery to a higher value by 100 cm., and a subsequent large reduction in organic content above about 80 cm.

Interpretation

The general interpretation advanced for these results is that the muds represent mainly the fine silts and some organic matter washed into the lake from the erosion of the surrounding basin. The coarser silts and sands from this erosion were deposited in the delta regions. It is assumed (cf. Pennington, 1943) that the rate of sedimentation in deep water has remained approximately constant throughout the period of deposition. The fluctuations in organic content and in nitrogen could thus reflect the variations in the amount of organic production on the drainage system and of humus and nitrogen in the surrounding soils.

It is obvious that many considerations are involved in accepting these assumptions. These will be more profitably discussed after all the evidence is marshalled, but it may be mentioned here that, of the nitrogen present, most (95 per cent.) is in organic combination and that the ratio of nitrogen to organic matter is that characteristic of terrestrial soils in Britain, and not the high value characteristic of planktonic material. The organic remains found in lake deposits may be of three main sorts. The organic matter derived from soils must come mainly from the upper horizons and consist largely of substances with a C/N ratio characteristic of terrestrial humus, about 12–15 in northern England. Organic material of planktonic origin would be expected to have a low C/N ratio, about 6 being the value given by Birge and Juday (cf. Misra, 1938). Detritus from terrestrial vegetation is also blown into a lake in autumn or carried in by streams. The remains of undecayed leaves can occasionally be detected in the mud. They preserve a characteristically high C/N ratio (+25). When dead leaves and twigs are carried into a lake by streams they collect in definite local zones around the stream deltas along with fine sand, and are not uniformly distributed over the lake bottom. The organic matter in the bulk of the lake mud

is very finely divided, or is included in the mineral particles. It thus appears on the evidence to possess the properties of soil humus, though other possibilities are obviously not precluded, and it is almost certainly modified by the addition of material of planktonic origin. Since, however, a productive lake in which the plankton effect might be high is also one which has fertile soils with nitrogen-rich humus, it is extremely difficult to distinguish the two effects.

Provisionally, therefore, the data are taken to reflect (*a*) the building up of nitrogen and organic matter in the soils of the drainage system at the end of, and after, the Ice Age with the Allerød interlude clearly represented at the start; (*b*) the establishment of a relatively stable high level of fixed nitrogen and of humus in the soils under forest cover; (*c*) the destructive effects of deforestation on the muds above the 200-cm. horizon, with a partial recovery about the 100-cm. horizon. The evidence on this basis suggests an early, fairly severe deforestation after the 200-cm. horizon, a recovery to a fairly stable position about the 100-cm. horizon, more destructive deforestation after this, and a recovery in recent years no doubt helped by cultivation, amenity planting, and sewage contamination.

The low nitrogen contents and faint silt bands about the 300-cm. horizon appear to be correlated with the so-called *Ulmus* horizon of pollen analysts, and are suggestive, to a varying degree in the two cores, of associated temporary woodland destruction about this time. Possible causes of this might be either human occupation or catastrophic changes, such as almost universal forest fires.

Mineral Analyses—Cores 3 and 4

The data are given in Tables 1 and 2 and the data for calcium and iron are presented in Fig. 2, the calcium on a much increased scale ($\times 20$) in order to bring out the pertinent effects.

The events which might be expected in such a series if we were dealing with soils would be, firstly the gradual hydrolysis of insoluble rock minerals, and secondly the leaching of cations in the order Na, K > Ca, Mg > Fe, Al. We should expect to find in a wet climate a diminution in calcium and an increase in iron as the soil colloids become leached, and thus an expected criterion of this type of change would be a fall in the calcium/iron ratio. It should be observed, however, that other tendencies might operate in lake muds, namely, there would be absorption of certain ions, notably of potassium and phosphate from the water (cf. Pearsall, 1920) and there might also be precipitation of insoluble salts (e.g. ferric compounds, cf. Mortimer, 1949) to a variable extent. The present analyses are unsuitable for following such changes even though the results may show signs of them.

It may be suggested that the analyses show that the sediments passed through five stages of development.

1. At first they were presumably almost unhydrolysed rock flour of low organic content, in which about one-fifth of the mineral matter now remains soluble in dilute acid, yielding, however, only small amounts of calcium and iron.

TABLE 1

Esthwaite Water: Analyses of Lake Muds (Core 3)

Depth (cm.)	*Loss on ignition % d.wt.*	*Nitrogen % d.wt.*	*m.e./100 g. ash*				
			Na	K	Ca	Mg	Fe
0–5	23·26	0·92	4·4	29·6	8·7	47·6	296
25–30	20·08	0·78	4·2	26·4	7·4	47·4	231
50–55	27·80	1·04	4·3	26·1	8·8	46·5	350
75–80	31·42	1·09	7·9	30·3	11·1	58·3	376
100–5	27·54	1·16	5·6	25·0	10·2	51·4	314
125–30	28·42	1·11	4·2	26·4	7·7	27·2	337
150–5	29·41	1·14	3·7	21·4	8·8	21·7	364
175–80	28·92	1·02	3·5	22·9	15·2	37·9	333
200–5	32·85	1·15	3·3	20·9	13·4	42·9	322
225–30	33·05	1·14	3·5	17·3	14·0	19·8	267
250–5	30·54	1·13	2·7	16·8	17·8	21·2	233
275–80	30·40	1·16	3·4	18·5	19·4	48·4	220
300–5	28·56	1·13	2·3	12·2	20·9	45·9	174
325–30	29·82	1·20	3·6	15·0	18·5	16·1	172
350–5	33·75	1·37	4·1	18·7	16·6	39·5	251
375–80	26·06	1·12	6·2	22·1	22·5	8·8	558
400–5	24·22	1·04	4·9	22·0	17·2	30·7	408
425–30	15·41	0·68	5·2	23·4	10·4	42·0	617
450–5	7·27	0·26	4·0	19·4	3·8	13·8	196
475–80	3·32	0·11	3·3	15·8	3·1	10·1	312
500–5	2·98	0·06	4·5	14·1	2·4	17·5	350
515–20	3·36	0·06	4·7	15·2	3·4	16·2	314

TABLE 2

Rydal Water: Analyses of Lake Muds (Core 4)

Depth (cm.)	*Loss on ignition % d.wt.*	*Nitrogen % d.wt.*	*m.e./100 g. ash*				
			Na	K	Ca	Mg	Fe
7	20·05	0·68	4·0	19·9	12·5	55·3	448
27	17·83	0·61	4·2	21·4	13·8	49·7	444
57	21·43	0·78	4·5	21·0	14·9	52·7	438
85	23·31	0·82	3·5	19·5	14·1	47·6	410
125	25·36	1·00	3·7	21·2	14·5	49·2	388
155	24·77	0·86	3·9	19·0	16·8	44·5	374
193–4	22·30	0·83	3·5	18·3	17·9	43·8	386
215	22·61	0·80	4·6	22·1	18·6	41·5	350
250	33·58	1·20	4·1	18·4	21·5	37·4	228
285	31·31	1·17	3·9	18·5	17·6	39·8	272
315	32·90	1.19	3·6	15·8	18·3	40·2	252
349	33·98	1·12	3·0	14·7	21·8	47·9	212
385	33·39	1·05	3·0	14·9	27·1	41·9	234
428	32·46	1·00	3·6	15·8	25·7	46·1	242
463	31·77	1·02	3·6	17·1	26·0	48·6	250
499–500	28·93	0·92	3·8	15·9	28·3	50·2	288
526	27·54	0·80	3·7	16·1	31·4	54·6	302
561–2	16·23	0·48	3·7	17·6	35·1	55·0	394

2. As the organic content rises the amounts of extractable calcium and iron increase up to a mud horizon of about 380 cm. below the core surface. This represents the period of forest development.

3. The amount of soluble matter then diminishes, but the ratio of calcium to iron is relatively high, but possibly tends to fall slowly. Between 370 and 250 cm. Ca:Fe averages 18·4:210 m.e.

4. In the region 200–20 cm. the calcium/iron ratio falls to a level of about 14:307 m.e. This represents approximately the period of early forest disturbance.

5. In the uppermost sediments, above 180 cm., the Ca:Fe ratio averages about 9:324. This represents a period of varying but generally progressive deforestation.

There is thus a general fall in the calcium/iron ratio in the upper sediments which agrees with the supposition that they represent soils showing progressive leaching. The evidence is in accordance with the idea that the tendency was in part a long-term trend, but the very rapid deterioration in zone 5 after initial deforestation is worth notice as it suggests a great acceleration of the process when the forest cover is broken down.

In drawing conclusions from these results we are influenced by the general characters of the Esthwaite basin. It is not mountainous and much of it is covered by drift both as eskers and also as layers of rather gravelly clays and loams. Where these have been examined at any depth up to 2 m. below the present soil surface they are now acid (pH 4–4·5) and evidently leached, a result perhaps to be expected with an annual rainfall of from 170 to 200 cm. Gorham (1958) has shown that the water from similar surface soils in this district may be hardly distinguishable from rain water in mineral content. The drifts originally must have had a much higher base status as they come partly from the Borrowdale volcanic rocks which may contain over 4 per cent. of calcium (Ward, 1876).

Apart from signs of late glacial solifluction, the erosion pattern of the basin shows that much of the material deposited in the lake has been derived from cutting back stream channels in the drifts on the steeper parts of the valley sides and from erosion of the upper soils, where apparently truncated profiles can be found. The coarse materials, mainly sandy, from these erosion sources have been deposited in the upper mile of the Esthwaite Valley and are not evident in the present lake except around the mouths of one or two small lateral feeders. The fine materials found in the deep water muds are not angular and do not show the other characters observed in the coarser sediments. The latter will be considered in detail elsewhere.

These changes are regional, as is shown, for example, not only by the data already given for Windermere (Pearsall and Pennington, 1947) but also by a similar series of analytical data from Rydal Water, another small adjacent lake. This differs from Esthwaite Water mainly in lying among steep slopes and high hills which bear hardly any drift. The increased erosion in the latter part of the post-glacial period was very clearly visible in the mud-core, for the upper 40 per cent. of the brown

mud was of a much lighter colour. The effect of deforestation on these steep slopes has evidently included the removal of soil into the lake, as is also suggested by some truncated soil profiles. The analytical data show, as a result, a much more marked fall in nitrogen content and loss on ignition in the upper sediments, though there is again an improvement at 125 cm. followed by further deterioration. Although the sediments start at a higher initial calcium level, possibly because this lake lies wholly on the Borrowdale Volcanic series, the calcium content diminishes progressively and the Ca/Fe ratio falls, markedly so after the beginning of the erosion sediments at 215 cm. It is evident that these contain much more iron than those deposited earlier.

Although this core is rather longer (the brown muds begin at a depth of just over 560 cm.), the general sequence of changes is very similar to that from Esthwaite Water in spite of the different type of country around the lake. Full details of the pollen history are not available, but the lighter muds above 215 cm. show the characteristic change to less tree and more grass-sedge pollen.

The general conclusions to be drawn from these analyses is that the lake sediments rather accurately reflect changes in the soils of the lake drainage system due to climatic trends and to alterations in vegetation cover associated with human activity.

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THE RED EARTHS AND THE COLLOIDS OF THE RED EARTHS

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Summary

The chemical composition of the soils and of the colloidal separates of twelve red earths from three widely differing locations in Italy has been determined. The red earths of southern Italy are characterized by low organic matter, little if any $CaCO_3$, and appreciable quantities of soluble salts. Those of northern Italy have opposite characteristics. The SiO_2/R_2O_3 ratios of the colloids range from 1·60 to 2·09 and bear no relationship to location or climatic factors.

It is concluded that similar pedogenetic processes have occurred throughout the Italian peninsula and are independent of geographical position or climatic conditions. In particular the SiO_2/R_2O_3 ratio of the colloids of the southern soils is not unusually low as has been suggested by other workers.

Introduction

THE origin, composition, and properties of the red earths of the Mediterranean regions have long been subjects of study and controversy. Many investigations of the problem have clearly shown that the red earths may not be identified only by their red colour. It has been suggested (Blanck, 1930; Reifenberg, 1933), without knowledge of the Italian soils, that the red earths may be characterized by a silica/sesquioxide ratio of approximately 2.

The term 'terra rossa' is of Italian origin, and the Italian soil formations of this kind are typical red earths. Twelve years ago Bottini and Lisanti (1948) made an extensive study of the Italian soils which were neither red nor developed under conditions typical for the production of red earth, but had a SiO_2/R_2O_3 ratio of approximately 2. It became apparent that a thorough study of this ratio in the red earths was necessary.

This paper reports on a study of the influence of climate on the origin of the adsorbed cations of the soils, and the chemical composition of the colloidal fraction of the red earths as a means of interpreting pedological processes.

Experimental

The soil samples used were taken from three different regions representing the most characteristic formations of the red earths. Three were taken in northern Italy in the region of Friuli, six in the region of Puglia, and three in southern Italy in the region of Sicily. A total of thirty samples was taken, twelve of which were finally selected as being the most representative of the various zones and types encountered.

Calcium carbonate was determined by the method of Hutchinson and MacLennan (1914), organic matter by Robinson's method (1927), and nitrogen by the Kjeldahl method. Phosphorus was determined by the Lorenz method (1912), potassium by the perchlorate method, and sodium as sodium uranyl magnesium acetate.

Results

Some chemical characteristics of several Italian red earths

The data (Table 1) show that the organic matter and nitrogen contents are very low in soils from southern Italy. This is an area of low rainfall and high temperatures. Calcium carbonate is generally absent. In the cooler, damp climate of northern Italy the effect of higher rainfall is seen in the lower soluble-salt content. The soils are all similar with respect to pH.

TABLE 1

Some Chemical Characteristics of Several Italian Red Earths

Soil no.	*Location*	*Calcium carbonate* %	*Organic matter* %	*Nitrogen* %	*Water-soluble salts* %	*pH*
	Northern Italy					
1	Tarcento	Absent	2·85	0·260	0·090	7·25
2	Gemona	,,	2·70	0·240	0·087	7·05
3	Cividale	,,	2·53	0·218	0·075	7·05
	Region of Puglia					
4	Foggia	,,	1·84	0·170	0·008	7·35
5	S. Severo	Trace	1·59	0·140	0·104	7·30
6	Cerignola	Absent	1·85	0·170	0·012	7·35
7	Bari	Trace	0·39	0·030	0·150	7·15
8	Bitetto	Absent	0·60	0·051	0·125	7·25
9	Mola	,,	0·75	0·070	0·120	7·20
	Extreme southern Italy					
10	Palermo I	,,	0·85	0·080	0·108	7·15
11	Palermo II	,,	0·59	0·050	0·105	7·30
12	Palermo III	,,	0·71	0·067	0·100	7·35

The chemical composition of the red earths (Table 2) shows a range of silica from 40 to about 60 per cent., alumina 16 to 29 per cent., and iron sesquioxide from 7 to 12·5 per cent. The content of alkaline earths is low, and of hygroscopic water high. Both phosphorus and sulphur are low.

Exchangeable cations were determined by the method of Mehlich (1948). Sufficient air-dry soil to give 0·5–2·5 m.e. exchange capacity was treated with $BaCl_2$ adjusted to pH 8·1 with triethanolamine.

The results are presented in Table 3.

TABLE 2

Chemical Composition of the Red Earths

Soil no.	*Location*	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	CaO %	MgO %	K_2O %	Na_2O %	P_2O_5 %	SO_3 %	$H_2O \pm 110°$ C. %
	Northern Italy										
1	Tarcento	48·98	21·54	9·84	2·18	0·74	1·36	1·02	0·08	0·13	14·12
2	Gemona	46·85	21·83	11·30	1·95	0·80	1·52	1·27	0·09	0·02	14·35
3	Cividale	46·58	20·71	10·86	2·05	1·50	1·70	1·09	0·07	0·02	15·39
	Region of Puglia										
4	Foggia	44·34	26·51	8·25	2·92	1·54	2·47	1·00	0·07	0·05	12·83
5	S. Severo	45·75	24·70	9·05	2·59	1·63	2·10	1·35	0·07	0·04	15·69
6	Cerignola	44·80	25·30	8·75	2·67	1·75	2·24	1·07	0·06	0·03	13·30
7	Bari	41·56	30·04	12·50	2·56	1·52	1·11	1·05	0·05	0·07	9·51
8	Bitetto	43·20	29·50	11·72	2·50	1·34	1·25	1·09	0·07	0·08	9·22
9	Mola	44·19	28·12	10·14	2·13	1·78	1·97	1·08	0·07	0·09	10·40
	Extreme southern Italy										
10	Palermo I	42·83	27·15	11·45	2·39	1·53	1·62	1·18	0·04	0·07	11·72
11	Palermo II	58·14	15·02	7·98	2·72	1·60	1·26	1·63	0·05	0·05	11·53
12	Palermo III	60·91	15·70	7·80	2·53	1·71	1·30	1·45	0·05	0·02	8·50

TABLE 3

Exchangeable Bases of the Red Earths

Soil no.	*Location*	*m.e. for 100 g. soils*					*Percentage distribution of exchangeable cations*			
		Ca	Mg	K	Na	*Sum*	Ca	Mg	K	Na
	Northern Italy									
1	Tarcento	28·55	4·44	0·46	4·52	38·15	74·83	11·64	1·68	11·85
2	Gemona	21·15	7·12	2·90	4·15	35·32	59·88	20·16	8·21	11·75
3	Cividale	18·18	4·11	3·46	4·45	30·20	60·20	13·61	11·46	14·73
	Region of Puglia									
4	Foggia	15·80	5·34	9·51	3·30	33·95	46·54	15·73	28·01	9·72
5	S. Severo	15·30	5·20	9·45	4·12	34·07	44·90	15·26	27·74	12·10
6	Cerignola	16·18	4·97	8·27	3·72	33·14	48·82	15·00	24·95	11·23
7	Bari	20·10	4·77	2·25	3·72	30·84	65·18	15·47	7·30	12·05
8	Bitetto	19·18	4·60	5·25	3·51	32·54	58·94	14·14	16·13	10·79
9	Mola	19·95	4·12	4·18	3·21	31·46	63·41	13·09	13·29	10·21
	Extreme southern Italy									
10	Palermo I	18·14	3·77	5·43	4·16	31·50	57·59	11·97	17·24	13·20
11	Palermo II	17·95	5·76	1·13	3·26	28·10	63·88	20·50	4·02	11·60
12	Palermo III	18·21	5·39	1·71	3·69	29·00	62·79	18·59	5·89	12·73

Separation of the colloidal fraction of the red earths

Exactly 250 g. soil was washed repeatedly to remove soluble salts. The soil was then transferred to a large porcelain dish and dispersed in distilled water containing a few drops of ammonia. The soil was triturated gently with a rubber pestle and allowed to settle for 24 hours. The supernatant liquid was decanted into a 30-litre glass vessel and the treatment of the residue was repeated until the supernatant liquid was clear. The suspended solids in the decanted liquids were kept in the dark for 33 days, after which the upper 10-cm. layer was removed by

siphon. The material in this portion was separated by means of Pasteur-Chamberlain filters. The air-dried colloid was then analysed chemically. The data are given in Table 4.

TABLE 4

Chemical Composition of Colloids of the Red Earths

Soil no.	*Location*	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	CaO %	MgO %	K_2O %	Na_2O %	$H_2O\pm 110°C.$ %
	Northern Italy								
1	Tarcento	37·62	26·55	13·57	2·76	1·99	0·70	1·15	15·65
2	Gemona	38·95	25·69	12·85	2·61	2·32	0·98	0·80	15·78
3	Cividale	40·12	27·91	11·51	2·70	1·80	0·81	1·14	13·98
	Region of Puglia								
4	Foggia	39·08	28·18	9·98	3·20	1·32	1·17	0·85	16·20
5	S. Severo	39·74	27·81	10·12	3·62	1·29	1·16	0·60	15·63
6	Cerignola	41·12	26·31	8·72	3·15	1·71	1·51	0·57	16·88
7	Bari	38·66	29·66	12·37	3·24	0·62	0·39	0·76	14·28
8	Bitetto	38·42	30·51	14·23	2·21	0·83	0·37	0·90	12·50
9	Mola	39·10	30·21	11·15	2·70	1·05	0·90	0·78	14·07
	Extreme southern Italy								
10	Palermo I	38·99	29·51	13·72	1·72	0·69	0·65	0·55	14·13
11	Palermo II	40·48	25·18	11·97	3·36	1·85	1·35	0·90	14·89
12	Palermo III	40·85	26·81	10·74	3·45	1·92	1·21	0·85	14·14

TABLE 5

Molecular Silica/Sesquioxide Ratios

Soil no.	*Location*	*Molecular ratio*			*pH*
		Fe_2O_3/Al_2O_3	SiO_2/Al_2O_3	$SiO_2/(Fe_2O_3+Al_2O_3)$	
	Northern Italy				
1	Tarcento	0·32	2·41	1·81	7·25
2	Gemona	0·31	2·58	1·96	7·05
3	Cividale	0·26	2·44	1·92	7·05
	Region of Puglia				
4	Foggia	0·22	2·35	1·93	7·35
5	S. Severo	0·23	2·43	1·97	7·30
6	Cerignola	0·21	2·66	2·19	7·35
7	Bari	0·26	2·21	1·75	7·15
8	Bitetto	0·29	2·14	1·65	7·25
9	Mola	0·23	2·20	1·78	7·20
	Extreme southern Italy				
10	Palermo I	0·29	2·19	1·70	7·15
11	Palermo II	0·30	2·17	2·09	7·30
12	Palermo III	0·25	2·58	2·07	7·35

Silica/sesquioxide ratios in the colloids

The data in Table 5 show that the SiO_2/R_2O_3 ratio varies from 1·65 to 2·09 and there is no correlation with pH of the soil. This is contrary

to Reifenberg's (1933) conclusion that the ratio should be about 2. Furthermore, no particular ratio is peculiar to any of the three regions of Italy studied. It appears, therefore, that similar pedogenic processes have taken place throughout the Italian peninsula.

It has been assumed by some investigators that in southern Italy there are climatic factors favourable for the development of lateritic-type soils with a low SiO_2/R_2O_3 ratio. This conclusion is not supported by the data presented here.

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COMPOSITION OF COLLOIDS IN THE SOILS OF ISRAEL

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Summary

By their chemical composition, the colloids from various types of soils in Israel may be grouped into three classes. According to their mineralogical composition the colloids represent various associations, two of which are conspicuous.

(*a*) Colloids with SiO_2/R_2O_3 ratio of 2·0–2·6. They are devoid of calcium carbonate, relatively poor in potassium and phosphorus, and content of organic matter is generally moderate. In the combination of clay minerals found, kaolin is predominant; in addition there are present illite, hematite, quartz, and, in some instances, montmorillonite. These colloids are characteristic of soils belonging to the Mediterranean red earths including terra rossas, brown Mediterranean soils, and brown-red sandy soils—leached soils of the humid and sub-humid regions, formed from hard limestone, dolomite, hard chalk, and kurkar.

(*b*) Colloids with SiO_2/R_2O_3 ratio of 3·6–5·2. Rich in calcium carbonate, potassium, and phosphorus, relatively poor in organic matter. In the association of clay minerals, montmorillonite is predominant; in addition there are also present illite, kaolin, and quartz. In some instances attapulgite was identified in appreciable quantities. The colloids also contain considerable quantities of calcite. The soils for which these colloids are characteristic were formed from soft chalk, marl, aeolian desert dust, and are found principally in the semi-arid and arid regions of Israel. They include rendzinas of the mountains and valleys, loess, aeolian sandy soils, and hamadas.

(*c*) Colloids with SiO_2/R_2O_3 ratio of 3·4–3·8. Most of them contain calcium carbonate, their potassium content is moderate, and they are relatively poor in phosphorus and organic matter. By their mineralogical composition these colloids resemble the combination in which montmorillonite is the principal clay mineral. They are characteristic of alluvial soils formed from alluvium of the Mediterranean red earths and rendzinas. The soils were developed under sub-humid and semi-arid climatic conditions.

IN the course of the soil survey carried out on Israel soils, a study of the nature of the soil colloids was conducted in order to supplement and clarify views on the origin, formation, and properties of various soil types.

Among the factors influencing the formation of the soils and determining their characteristics, the parent material and the climate are of prime importance. The variation in parent material, climate, and density of vegetation cover are great in the different regions of Israel.

It may be noted that under identical humid and sub-humid climatic conditions on hard limestone or dolomite, terra rossa soils free of lime develop, and on chalk and marl rendzina soils rich in lime are formed. On the other hand under arid climatic conditions coarse desert calcareous soils develop from the same parent material which produces terra rossas in the humid and sub-humid regions.

Changes occurring in the parent rocks during the course of the weathering process resulting in the formation of soils with very different properties, naturally influenced the character of their colloids.

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The object of this study was to determine the properties of colloids found in the various soils. For this purpose samples of colloids were separated from the principal soil types in Israel. The chemical and mineralogical composition of the colloids was determined, and the colloids were classified in accordance with their properties.

Methods

Soil samples, from which the colloids were separated, were collected from the A horizon of the profiles. Separations were made from aqueous soil suspensions. The chemical constituents of the colloids, after fusion, were determined according to the official and tentative methods of A.O.A.C. (1955). Total organic matter was determined by the Tyurin (1936) modification of the Schollenberger (1927) method.

Mineralogical composition of the colloids was determined by differential thermal and X-ray phase analyses. The D.T.A. apparatus was patterned after that of Norton (1939). Rate of heating was 11° C. a minute. A nickel block was used as the specimen holder. X-ray analysis was performed with a Guinier camera after Wolf (1948), with Cu $K\alpha$ radiation. The apparatus was a production of 'Nonius', Delft, Holland.

Soils Used in Colloids Investigation

The soils, from which colloids were separated and investigated, are of residual, alluvial, and aeolian origin. They developed under various climatic conditions—humid, sub-humid, semi-arid, and arid (Ashbel 1945; Rosenau, 1947)—and formed from different parent material as limestone, chalk, marl, kurkar, basalt, aeolian dusts, and alluvium of various sources. The soils, according to their genesis and properties, are classified into six groups: Mediterranean red earths, rendzinas, loess and loess-like soils, sandy soils, hamadas, and alluvial soils. The groups of soils are subdivided into soil types. Most of the soils used for colloid separation were virgin.

Chemical Composition of the Colloids

The chemical composition of the colloids from various types of soils differ considerably (Tables 1, 2, 3). According to their composition they may be grouped into:

A. Colloids that do not contain calcium carbonate, found in soils formed from hard limestone, hard chalk, kurkar, and basalt. These soils are: terra rossa, brown Mediterranean soils, brown-red sandy soils, and basaltic soils—all belonging to Mediterranean red earths.

B. Colloids containing calcium carbonate, found in soils formed from soft chalk, marl, aeolian desert dust, or from desert soils. These colloids were separated from rendzinas, loess, and hamadas.

C. Colloids found in alluvial soils of various origin. These soils were developed principally from Mediterranean red earths alluvium and rendzina alluvium, frequently consisting of a mixture of these two sources in various proportions.

The colloids of various soils vary principally in their silicon, aluminum, calcium, and iron contents.

TABLE 1

Soils Used in the Colloid Investigation

Soil no.	*Locality and region*	*Climate*	*Group*	*Type*	*Origin*
1	Metulla, Upper Galilee Mountains	Humid	Mediterranean red earths	Terra rossa	Hard limestone
2	Eilon, Upper Galilee Mountains	Humid	" "	" "	" " and dolomite
3	Ramot Naphtali, Upper Galilee Mountains	Humid	" "	" "	Hard limestone
4	Safad, Upper Galilee Mountains,	Humid	" "	" "	" "
5	Ma'ale Hahamisha, Jerusalem Mountains	Sub-humid	" "	" "	" "
6	Dalia, Ephraim Mountains	Sub-humid	" "	Brown Mediterranean soil	Hard chalk
7	Kefar Tabor, Lower Galilee Mountains	Semi-arid	" "	Basaltic soil	Basalt
8	Rehovot (A), Shefela	Sub-humid	" "	Brown-red sandy soil	Kurkar
9	Tel Zur, Hasharon	Sub-humid	" "	Brown-red sandy soil	Kurkar
10	Rehovot (B), Shefela	Sub-humid	" "	Brown-red sandy soil	Kurkar
11	Hanita, Upper Galilee Mountains	Sub-humid	Rendzinas	Mountain rendzina	Chalk
12	Kefar Uriya, Judea	Sub-humid	"	Mountain rendzina	Marl
13	Messilot, Beit Shean Valley	Semi-arid	"	Valley rendzina	Lissan marl
14	Beit Shean, Beit Shean Valley	Semi-arid	"	Valley rendzina	Lissan marl
15	Ashdot Ya'aqov, Jordan Valley	Semi-arid	"	Valley rendzina	Lissan marl
16	Beersheba, Northern Negev	Arid	Loess and loess-like soils	Aeolian loess	Aeolian dust
17	Gevulot, Northern Negev	Arid	Sandy soils	Sandy aeolian soil	" "
18	Ein Hozev, Southern Negev	Arid	Hamadas	Mountain Hamada	Limestone-flint
19	Ein Harod, Eastern Yizreel Valley	Semi-arid	Alluvial soils	Brown grey alluvial hydromorphic soil	Alluvium of Mediterranean red earths and rendzinas
20	Nahalal, Western Yizreel Valley	Sub-humid	"	Brown-greyish alluvial soil	Alluvium, principally of Mediterranean red earths origin
21	Kefar Yehoshua, Western Yizreel Valley	Sub-humid	"	Brown-greyish alluvial soil	Alluvium, principally of Mediterranean red earths origin

TABLE 2

Chemical Composition of Colloids from Soils of the Mediterranean Red Earths Group (%)

Type of soil	*Terra rossa*					*Brown Mediterranean soil*	*Brown red sandy soil*		*Basaltic soil*
Locality	*Metulla*	*Eilon*	*Ramot Naphtali*	*Safad*	*Ma'ale Hahamisha*	*Dalia*	*Rehovot A*	*Rehovot B*	*Kefar Tabor*
Constituents									
SiO_2	41·56	41·46	43·44	47·40	48·69	46·59	48·78	45·26	50·05
Fe_2O_3	14·36	13·75	11·27	12·35	12·74	12·34	12·48	12·85	14·20
Al_2O_3	25·65	25·53	28·10	25·99	23·37	22·88	26·33	25·69	17·11
CaO	2·03	2·14	1·49	1·96	1·84	2·28	1·51	1·20	3·12
MgO	2·78	3·16	1·78	2·83	2·37	3·34	1·78	2·34	4·05
K_2O	0·23	0·67	0·28	0·24	0·85	0·57	0·92	1·30	0·10
Na_2O	0·75	0·65	0·97	1·05	0·60	0·67	0·54	1·16	0·26
P_2O_5	0·32	0·19	0·10	0·20	0·14	0·12	0·18	0·16	0·17
SO_3	0·60	1·24	1·30	0·38	0·56	0·92	0·23	0·36	2·85
CO_2	0·18	None	None	None	None	None	None	None	None
Organic matter	2·95	3·26	1·23	2·09	1·71	2·59	0·89	..	1·52
Combined water	7·78	8·02	9·52	6·10	6·76	7·81	6·61	10·87	7·29
N	0·30	0·31	0·15	0·29	0·18	0·31	0·10	0·19	0·17
C/N	5·7	6·1	4·8	4·2	5·5	4·8	5·2	..	5·2
pH	6·9	6·3	6·0	6·6	7·0	6·6	6·5	..	6·8
$SiO_2/Al_2O_3+Fe_2O_3$	2·0	2·0	2·1	2·4	2·6	2·6	2·4	2·3	3·2
SiO_2/Al_2O_3	2·7	2·8	2·6	3·1	3·5	3·4	3·1	3·0	4·9

TABLE 3

Chemical Composition of Colloids from Rendzina, Loess, Hamadas, and Sandy Soils (%)

Type of soil	*Mountain rendzina*		*Valley rendzina*			*Loess*	*Sandy aeolian soil*	*Mountain hamada*
Locality	*Hanita*	*Kefar Uriya*	*Messilot*	*Beit Shean*	*Ashdot Ya'aqov*	*Beersheba*	*Gevoulot*	*Ein Hozev*
Constituents								
SiO_2	20·06	40·23	39·95	19·28	44·24	44·47	49·40	48·82
Fe_2O_3	3·55	5·88	7·04	2·48	8·55	8·44	7·94	9·11
Al_2O_3	2·43	11·21	12·22	4·65	15·00	15·50	15·74	14·54
CaO	35·52	14·79	14·64	32·12	12·69	10·43	7·99	6·91
MgO	2·58	3·13	4·46	3·69	3·06	4·75	3·11	4·56
K_2O	0·41	1·27	2·25	0·94	1·19	1·25	1·20	0·08
Na_2O	0·26	0·85	0·30	0·32	0·18	0·24	0·33	0·30
P_2O_5	0·93	1·90	0·19	0·45	1·05	0·27	0·22	0·61
SO_3	0·11	0·79	0·50	1·11	0·36	0·80	0·57	1·23
CO_2	27·74	9·61	9·41	22·87	6·50	7·59	6·20	4·91
Organic matter	..	1·38	1·64	2·31	1·30	1·18	1·65	0·87
Combined water	6·22	9·82	6·97	9·57	6·58	5·07	5·39	6·73
N	..	0·15	0·19	0·23	0·13	0·17	0·18	0·07
C/N	..	5·5	5·0	5·8	5·8	4·0	5·3	7·2
pH	..	7·8	7·8	7·7	7·7	7·7	7·7	8·2
$SiO_2/Al_2O_3+Fe_2O_3$	7·2	4·6	4·1	5·2	3·7	3·6	4·0	4·1
SiO_2/Al_2O_3	14·0	6·1	5·5	7·0	5·0	4·9	5·3	5·7

TABLE 4

Chemical Composition of Colloids from Alluvial Soils (%)

Type of soil	*Brown-grey hydromorphic alluvial soil*	*Brown-greyish alluvial soil*	
Locality	*Ein Harod*	*Nahalal*	*Kefar Yehoshua*
Constituents			
SiO_2	43·08	49·38	52·24
Fe_2O_3	8·24	10·33	11·61
Al_2O_3	13·85	17·93	20·73
CaO	10·85	7·32	3·14
MgO	4·81	3·22	3·10
K_2O	0·95	0·49	0·88
Na_2O	0·28	0·13	0·21
P_2O_5	0·19	0·14	0·09
SO_3	0·39	0·44	0·62
CO_2	7·31	3·56	None
Organic matter	1·29	1·20	1·45
Combined water	8·29	6·50	5·45
N	0·15	0·13	0·17
C/N	5·0	5·3	4·9
pH	7·7	7·6	7·1
$SiO_2/Al_2O_3+Fe_2O_3$	3·8	3·4	3·4
SiO_2/Al_2O_3	5·3	4·7	4·3

Mineralogical Composition of the Colloids

By their mineralogical composition the colloids comprise various associations. Of these, two prevailing associations of specific minerals are conspicious, each being characteristic for a distinct group of soils (Table 5).

A. An association with kaolin as the main clay mineral; the other components are illite, hematite, quartz, and occasionally montmorillonite.

This combination of minerals is characteristic to terra rossas, brown Mediterranean soils, brown-red sandy soils derived from hard limestone, hard chalk and calcareous sandstone respectively—all belonging to the Mediterranean red earths. The kaolin of the colloidal fraction of these soils comprises more than one-half of its total mineral content. Illite was found, in limited quantities, in most of these soil types and quartz is present in all without exception. No montmorillonite was identified in most samples of colloids from the Mediterranean red earths and, where found, the quantities were small. In some soils the presence of hematite was established.

B. In the second association of minerals, montmorillonite is dominant; other minerals present are: illite, kaolin, and quartz. In some instances attapulgite in appreciable quantities was also found. Calcite content is often found to be very high. This combination of minerals is characteristic of both mountain and valley rendzinas, loess soils, and sandy aeolian soils. These soils were formed under dry climatic conditions.

TABLE 5

Mineralogical Composition of Colloids from Various Soil Types

Locality	*Group*	*Type*	*Minerals (in order of their prevalence)*
Metulla	Mediterranean red earths	Terra rossa	Illite, kaolin, quartz
Eilon	" "	" "	Kaolin, hematite, quartz, montmorillonite
Ramot Naphtali	" "	" "	Kaolin, illite, quartz
Safad	" "	" "	Kaolin, illite, quartz
Ma'ale Hahamisha	" "	" "	Kaolin, montmorillonite, illite, quartz, hematite
Dalia	" "	Brown Mediterranean soil	Kaolin, illite, quartz
Rehovot	" "	Brown-red sandy soil	Kaolin, illite, quartz
Tel Zur	" "	" "	Kaolin, hematite, quartz, montmorillonite
Kefar Uriya	Rendzinas	Mountain rendzina	Montmorillonite, calcite, illite, kaolin, quartz
Messilot	"	Valley rendzina	Montmorillonite, calcite, attapulgite, illite, kaolin
Beit Shean	"	" "	Montmorillonite, calcite, attapulgite
Ashdot Ya'aqov	"	" "	Montmorillonite, illite, calcite, kaolin, quartz
Beersheba	Loess	Aeolian loess	Montmorillonite, illite, calcite, kaolin, quartz
Gevulot	Sandy soils	Aeolian sandy soil	Montmorillonite, illite, quartz, calcite, kaolin
Ein Harod	Alluvial soils	Brown-grey alluvial hydromorphic soil	Montmorillonite, attapulgite, illite, calcite, kaolin, quartz
Nahalal	" "	Brown-greyish alluvial soil	Illite, montmorillonite, quartz, kaolin, calcite
Kefar Yehoshua	" "	" "	Montmorillonite, illite, kaolin, quartz

As a rule they contain various quantities of calcium carbonate, and in some soils the lime content is very high.

Among soils containing montmorillonite as their principal clay mineral are also included the alluvial soils with various contents of calcium carbonate. Types of minerals found in the colloids of alluvial soils are rather similar to those found in rendzinas.

In addition to montmorillonite, the dominant mineral, the alluvial soils contain illite, calcite, kaolin, and quartz in various quantities. Illite occupies, quantitatively, the second place among the minerals. It should be noted that the alluvial soil from Ein Harod, in addition to the other clay minerals, contains also attapulgite; in its mineralogical composition this soil resembles the rendzina soils of the neighbouring Beit Shean Valley where attapulgite was also found.

Discussion

From most of the soils belonging to the Mediterranean red earths group, the calcium carbonate was completely washed away and no

calcite was found in their colloids. The sesquioxides in these colloids comprise a relatively high quantity. The $SiO_2/(Al_2O_3+Fe_2O_3)$ ratio in the terra rossas is not constant; it depends, apparently, on the climatic conditions prevailing in the region in which the soil was formed. Reifenberg (1947) has found wide fluctuations of these ratios in terra rossas. The $SiO_2/(Al_2O_3+Fe_2O_3)$ and SiO_2/Al_2O_3 ratios in the colloids separated from basaltic soil were higher than those ordinarily found in the colloids of other soil types of the Mediterranean red earths group, which includes also the basaltic soils.

This phenomenon may have its explanation in the fact that the basaltic soil was formed in a semi-arid region. It can be assumed that under such climatic conditions the silica/sesquioxides and the silica/alumina ratios are much higher than those found in the colloids from basaltic soils of sub-humid and humid regions, from which the other soil types of the Mediterranean red earths group were investigated.

The small quantities of potassium found in the colloids can also be ascribed to the action of leaching. Potassium content was found to be very low in colloids from terra rossa, and especially from soils of this type that were formed in the more rainy regions. Colloids from the Mediterranean red earths are similarly poor in phosphorus. Deficiency of these essential plant nutrients may become more pronounced in irrigated soils of this group. The colloids of soils of this group are relatively rich in organic matter as well as in nitrogen. It should be noted that the percentage of organic matter in the colloids from terra rossas and brown Mediterranean soils is lower than in the soils themselves from which the colloids were separated. C/N ratio in the colloids is lower than that found in the soils; it is 4–6 in the colloids and 7–9 in the soils.

In soils formed from limestone in the arid regions, where the leaching factor is very limited and the weathering is principally of physical nature, calcium carbonate very often remains in the soil to a large extent and is, consequently, also present in the colloidal fraction.

Colloids of soils developed from soft calcareous formations, even under humid–sub-humid conditions, are generally rich in calcium carbonate. In many instances the percentage is very high. The properties of water absorption and retention and the property of swelling of the soft chalky and marly rocks, limit the possibilities of water percolation and leaching in the rainy season. The calcium carbonate dissolves in the water containing CO_2 and reprecipitates in the weathered material with the evaporation of water.

Under these specific conditions of soil formation, namely of rendzinas, loess, and hamadas—the colloids formed are poor in sesquioxides, although in their silica content they at times resemble colloids of the Mediterranean red earths. The silica/sesquioxide ratio is thus higher in the colloids of these soils. Potassium and phosphorus compounds were well preserved in the colloidal fractions. The colloids of the rendzinas, aeolian soils, and hamadas were quite conspicuous for the appreciable content of these nutrient constituents.

The colloids from rendzinas and aeolian soils in the semi-arid and arid

regions in many instances contain higher quantities of organic matter than in the soil from which the colloids were separated. The C/N ratio in the colloids was found to be lower (4–6), than that of the soils (6–13).

The composition of colloids from alluvial soils was found to be non-uniform; some are lacking, others are poor, and still others are rich in calcium carbonate. By their silica/sesquioxides ratio the colloids of these soils occupy an intermediate position between the colloids of the Mediterranean red earths and the rendzinas. The colloids from the alluvial soils contain moderate quantities of potassium and are relatively poor in phosphorus. Percentage of organic matter in the colloids is lower than in that from Mediterranean red earths and mountain rendzinas. The C/N ratio is smaller than in the soils; the values are 5 for the colloids and from 7 to 9 for the soils.

It should be noted that the C/N ratio of approximately 5 is almost a constant for all colloids separated from soils that differ in their chemical composition and have been formed under extremely different climatic conditions. The C/N ratio of the soils from which the colloids were separated, varied within the limits of 6–13.

Kaolin is characteristic and is the dominant clay mineral of soils in which leaching, as a formation factor, has played a significant role. These soils belong to the Mediterranean red earths group. They also contain illite. The presence of hematite in some soil samples of this group was established. Barshad *et al.* (1956) found in a terra rossa soil of Galilee, montmorillonite in addition to kaolin; illite was not present. According to Yaalon (1955), montmorillonite is the dominant clay mineral in the terra rossa of Israel; in addition to it, illite and kaolin were also found; the sandy brown-red soil contains kaolin as the main clay mineral; illite was also identified, as well as limited quantities of montmorillonite. Montmorillonite present in the parent rock of terra rossa is apt in the course of weathering to turn into kaolin (Grim, 1942). Limited quantities of montmorillonite were found in samples of terra rossas and sandy brown-red soils, as our investigation shows. The occurrence of montmorillonite among the other clay minerals, in terra rossas, requires further clarification. The presence of this clay mineral in terra rossa is generally dependent upon the climatic conditions under which the type of soil was formed. In regions of low precipitation in which terra rossa is still developing, greater quantities of montmorillonite may be found in these soils. Colloids examined in the present investigation were separated from soils in regions of heavier precipitation. Hosking (1941) states that from the same parent rock under different conditions of climate, topography, and time, both soils containing kaolin and soils containing montmorillonite can develop. According to Muir (1951) kaolin is the typical clay mineral in terra rossa. In the terra rossa of Spain and Western Africa illite was found to be the dominant clay mineral; montmorillonite was not detected (Muñoz, 1953). Cecconi (1955) found that in the soils of Italy illite is the main clay mineral, mostly associated with kaolin. Norrish and Rogers (1956) defined illite and kaolin as the main clay minerals in terra rossa of

Australia. Michand *et al.* (1946) identified palygorskite in terra rossas of Southern France.

Soils in which montmorillonite is the dominant clay mineral belong to the rendzina and loess groups. The presence of calcite, frequently in considerable quantities, was found in colloids from these soils; illite was found in relatively appreciable quantities and also some limited quantities of kaolin. In the rendzinas of the Beit Shean Valley attapulgite was identified.

In a number of calcareous soils, appearing to be rendzinas, and also in a loess soil, Barshad *et al.* (1956) found montmorillonite and attapulgite to be among the principal clay minerals. Calcite was also present in notable quantities; no illite was identified. According to another source (Yaalon, 1955) it appears that in a lissan marl soil, defined in our investigation as valley rendzina, the principal minerals are montmorillonite and kaolin; illite, palygorskite, and calcite were detected in smaller quantities. According to Grim (1953), quoting the work of Knox, rendzinas contain illite, kaolin, and montmorillonite in various quantities; he further adds that illite and montmorillonite are the principal clay minerals in soils of arid regions. Winters and Simonson (1951) likewise claim that these two clay minerals are characteristic of desert soils. As mentioned, montmorillonite, illite, and also calcite were found to be the principal minerals in the colloidal fractions of our soils in the semi-arid and arid regions. Montmorillonite and illite, and at times calcite, are also found in the heavy, alluvial, poorly drained soils of the sub-humid regions.

In alluvial soils the presence or predominance of one or another clay mineral is determined by the source supplying the alluvial material. It would seem that soil material transported to the valleys and plains from the regions where the Mediterranean red earths prevail, was not mature to the same degree as we find it today in the mountains as terra rossa or brown Mediterranean soil. The mineralogical composition of the colloidal fraction of alluvial soils was also influenced by specific conditions under which these soils were developed. The rate of maturation of the thick layers of alluvial material was very slow as a result of poor drainage and restricted leaching. Calcium carbonate was retained in the soils to a smaller or greater measure. Montmorillonite is the characteristic clay mineral of these soils, as it usually is in calcareous soils of other groups in more arid regions. It is suggested that the presence of calcium favours the formation of montmorillonite (Grim, 1953).

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AN INTRODUCTION TO THE SOILS OF THE SOUTH-EASTERN PORTION OF THE AUSTRALIAN ARID ZONE

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Summary

Seven soil regions, each of which is dominated by soils belonging to one or two great soil groups, are defined and mapped. The outstanding feature is the presence of a variety of soils with widely differing characteristics. The soils are deeper, have more profile differentiation and are finer-textured than those in most arid regions and are frequently overlain by currently-forming deposits of wind-transported materials. Because the vegetative cover is better developed and there are only small areas of rocky hills and bare rock pediments, water erosion and deposition are not as prominent as in other arid areas.

Introduction

THIS publication is the first of a series of papers dealing with the soils of two extensive and representative areas in the south-eastern portion of the Australian arid zone (Fig. 1). The soils of this region have not been investigated to any great extent in the past. Generalized soil maps prepared by Prescott (1931, 1944) and Blake (1938) included the whole or portions of it and reconnaissance surveys have been carried out in the Simpson Desert (Crocker, 1946) and north-western South Australia (Jessup, 1951). Detailed soil surveys have been published by Crocker and Skewes (1941) and Jackson (1957) of a small area in South Australia. Laboratory analyses of the soils discussed in the present paper are given by these earlier workers and by Prescott and Skewes (1938). In addition Whitehouse (1940) discussed the lateritic soils of western Queensland.

Climate

The climate is characterized by low and unreliable rainfall with intermittent periods of drought. Within the areas investigated the lowest rainfall (less than 5 in. average annual) occurs in the Lake Eyre region; this, in fact, is the driest part of Australia. Rainfall gradually increases to the south and east of this desert area, reaching a maximum of slightly more than 9 in. per annum at Port Augusta in the south, 13 in. at Cobar in the south-east, and 12½ in. at Cunnamulla in the east. There is no marked seasonal incidence, as the region lies between the monsoonal (summer rain) and 'antarctic' (winter rain) systems, and may receive rain from either.

Rainfall effectiveness is reduced by the occurrence of many light rains which, particularly during droughty times, do not penetrate to a sufficient depth to be available to plant roots. Thus Osborn, Wood and Paltridge (1935) from observations in north-eastern South Australia, concluded that falls of less than a quarter of an inch were ineffective during a dry period. On this basis only a third of the annual rainfall of this area is

effective. However, heavy and very heavy falls of rain do occur in the arid zone particularly during the summer months (Jackson, 1958).

Mean annual temperatures range from 64° F. to 71° F., the highest temperatures occurring in the north. There is a wide divergence between mean maximum and minimum temperatures and a wide diurnal range of temperature. At Koonamore (Osborn, Wood, and Paltridge, 1935) the average annual diurnal range is 30° F. The diurnal range is greatest

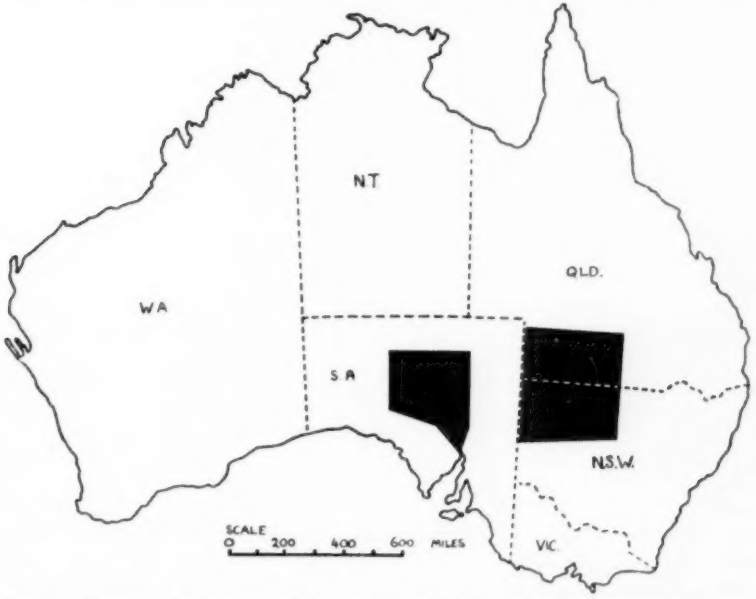

FIG. 1. Showing the location of the areas in which investigations were carried out.

during the summer months. For example, at Yudnapinna the mean diurnal range exceeds 40° F. for the months September to January inclusive.

Average annual evaporation ranges from about 70 in. in the south, for example Port Augusta and Cobar, to more than 100 in. north-west of Thargomindah (see Commonwealth Meteorological Bureau map). At Yudnapinna, where the annual average is 96 in., mean evaporation for the period November to March inclusive exceeds 10 in. per month.

The whole of the region lies within the 'mild arid' zone of Meigs (1953). His world map of arid homoclimates indicates that parts of Saudi Arabia and north-west (coastal) Africa have a comparable rainfall and temperature régime.

The Landscape

Vast plains are the dominant feature of the landscape; they range from a few feet below sea-level around Lake Eyre to a maximum of

about 500 ft. above sea-level. Isolated, more or less flat-topped ('tent') hills, groups of 'tent' hills, and plateaux rise abruptly above the plains in some areas to heights usually varying between 100 and 300 ft. (Jessup, 1960).

In the vicinity of the plateaux and plateau remnants are dissected pediments which, with increasing distance, gradually become gently undulating and ultimately merge with plains consisting of alluvial and lacustrine sediments that were deposited in earlier extensive internal drainage basins (Fig. 2). Sometimes, for example south of Lake Cadibarrawirracanna, the pediments are exposed, but they and the old lacustrine and alluvial sediments are usually buried beneath deposits of wind-distributed materials.

A characteristic feature of the old lacustrine basins is the presence, within them, of large numbers of playa lakes; some of these are shown in Fig. 3 but in addition there are many smaller ones. The playa depressions are the present drainage basins; although they occasionally contain water for short periods, they are normally dry. Many of the playas have well-developed salt crusts; these are popularly referred to as saltlakes. Lake Eyre, the largest playa, is approximately 25 ft. below sea-level and 4,000 sq. miles in area and the intermittently-flowing streams leading into it drain some 400,000 sq. miles of country (Fenner, 1952).

The depressions occupied by the playa lakes are, partly or entirely, wind-excavated hollows. King (1956) demonstrated that the Lake Eyre playa was formed as a result of removal by wind of Quaternary sediments that had accumulated in a vast lacustrine basin. Characteristic features of this and other playas are the shallow depth (Madigan, 1930; Bonython, 1956) or absence (see Jutson, 1934) of unconsolidated sediments in their beds. Some of the materials removed from the playa depression may accumulate to form a lunette along the leeward margin of the playa, and the sand fractions accumulate on the adjacent plains to form sand-ridges (Fig. 2). Sometimes remnants of the old lacustrine sediments have survived deflation and form 'islands' in the playas (Fig. 2).

In addition to large numbers of ephemeral streams which terminate in internal drainage basins the arid zone is traversed by a few permanently-flowing streams, such as the River Darling, which have their headwaters in the higher rainfall country beyond the arid zone. Along the permanent streams and the lower portions of the ephemeral streams floodplains, frequently of considerable extent, are developed.

In addition to the plateaux, a few low mountain ranges of small extent rise above the plains; the highest peak, Mt. Robe (1,556 ft. above sea-level), occurs in the Barrier Range. Flanking the ranges are areas of undulating uplands which are also characterized by the presence of buried pediments.

The Soil Regions

The areas investigated have been divided into a number of distinct soil regions (Figs. 3 and 4). Each region is dominated by soils belonging

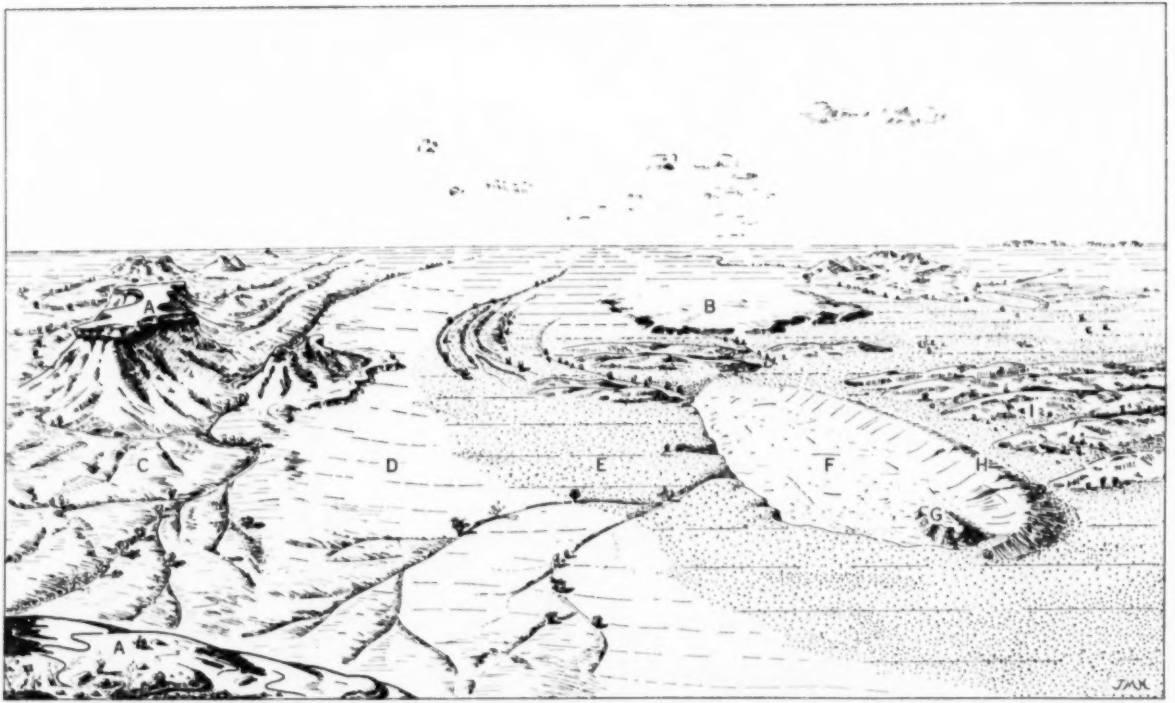

FIG. 2. Diagram, compiled from photographs and field sketches, of a typical desert landscape. A and B, plateau remnants of two distinct land surfaces. C, dissected pediments. D, gently-undulating pediments. E, alluvial and lacustrine basin plains. F, playa lake. G, 'island' (remnant of lacustrine sediments). H, lunette. I, area of sand-ridges.

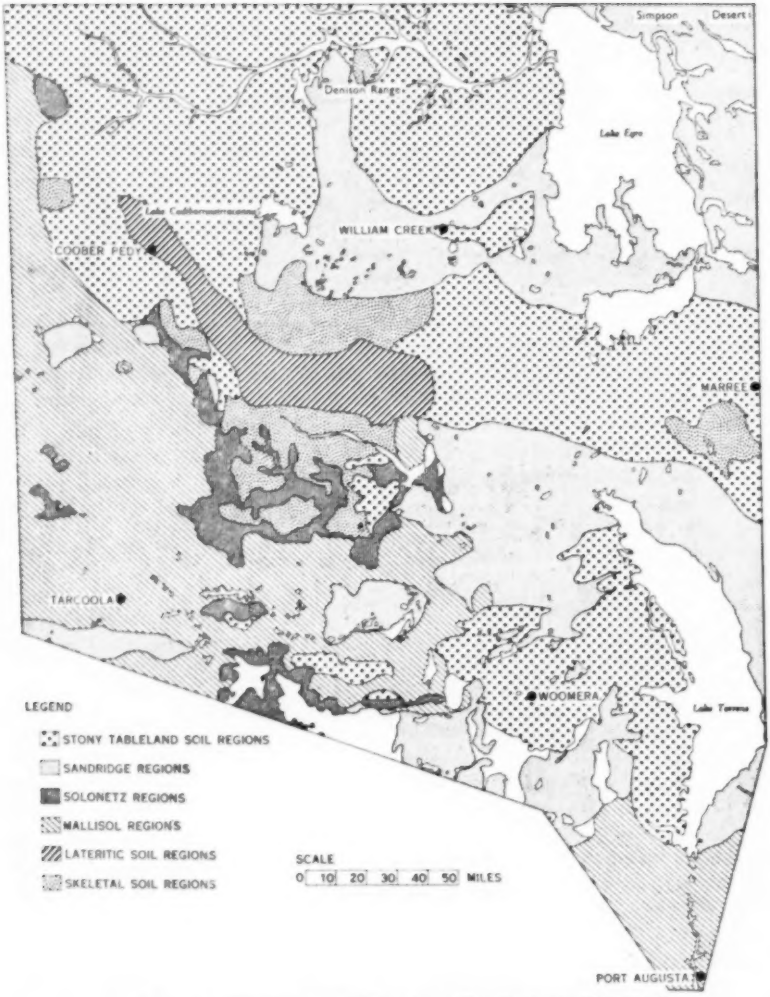

FIG. 3. Map showing soil regions (South Australian area).

to one or two great soil groups, but may include minor areas of soils belonging to other groups.

The stony tableland soil regions

In these areas stony tableland soils (Jessup, 1951) are dominant, but there are minor occurrences of grey soils of heavy texture (Prescott, 1944) on the river floodplains, soils that are similar to grey-brown and

red calcareous desert soils as defined by Stephens (1956) and truncated lateritic soils associated with 'tent' hills.

The stony tableland soils are fine-textured, gypseous and saline throughout practically the whole profile, but usually contain only small amounts of carbonate. The surface of the stony tableland soil layer has a well-developed micro-relief due to the presence of scattered irregular-

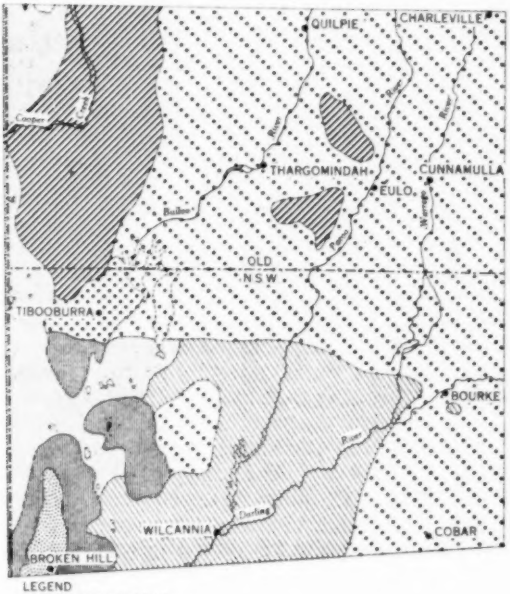

FIG. 4. Tentative map of soil regions (New South Wales–Queensland area).

shaped depressions. On sloping ground each depression has a mound along its lower margin. The depressions are commonly 3 to 10 yds. across and 6 to 24 in. deep, while the mounds are 6 to 18 in. high. The depressions may be 4 to 35 yds. apart. Between the depressions the soil surface is completely covered with a stone pavement and stone is usually restricted to the upper few inches of the profile. In the depressions themselves most of the stones are not at the surface, but are buried in the upper few inches of the profile. Jackson (1957) has pointed out that the origin of this peculiar stone pattern is one of the most puzzling features of the Australian arid zone.

Trees are absent from the stony tableland soil regions except along drainage lines; in fact vegetation of any kind is normally confined to the depressions where low-growing shrubs, particularly bladder saltbush (*Atriplex vesicaria*[1]), are the dominant plants (Jessup, 1951). Although the inter-depression areas are generally devoid of plants, the soils that occur there are protected from wind erosion by the surface stone pavement.

The mallisol regions

South of the stony tableland soil regions is a vast area of plains characterized by highly calcareous soils. The dominant soils are mallisols (Northcote, 1956) and soils that are similar to grey-brown and red calcareous desert soils as defined by Stephens (1956). There are minor occurrences of grey and brown soils of heavy texture on river floodplains, solonetz, stony tableland soils, sand-ridges, and truncated lateritic soils associated with 'tent' hills.

The mallisols are sands to sandy loams to varying depths from the surface, below which texture gradually rises to sandy clay; they are also leached of carbonate in the upper portion of the profile, but contain large amounts at depth. The carbonate occurs as nodules, in pockets (in amorphous form) and in the fine earth.

The soils that are similar to the grey-brown and red calcareous desert soils contain large amounts of carbonate in the fine earth and are commonly coarse to moderately coarse-textured throughout the profile, but may be medium-textured at depth.

Throughout the mallisol regions the two great soil groups are distributed in a random fashion; no satisfactory explanation has been advanced to account for this distribution.

These calcareous soils support rather open woodland vegetation (Beadle, 1948; Jessup, 1951; Crocker and Skewes, 1941) consisting of low trees of the order of 15 to 25 ft. in height, beneath which there may be a layer of low shrubs. During droughts the ground between the shrubs and trees is bare, but following rains is covered with herbaceous vegetation. The soils are subject to erosion by wind during droughty periods.

The red earth regions

East of the stony tableland soil regions is an extensive area of plains on which the dominant soil is red earth. There are minor occurrences of calcareous red earths (Stephens, 1956), brown soils of light texture (Prescott, 1944), and truncated lateritic soils associated with 'tent' hills. In addition the red earth plains are intersected by extensive floodplains, along streams like the Warrego, Paroo, and Bulloo, on which grey and brown soils of heavy texture and red-brown earths occur.

In the red earths there is a gradual rise in texture with depth, commonly from loam or clay loam in the upper part of the profile to sandy

[1] The nomenclature of species used in this paper is that of J. M. Black's *Flora of South Australia* (2nd edition).

clay. They have an acidic reaction (pH 5·0 to 6·5) throughout most of the profile but may be mildly alkaline at depth. No attempt, as yet, has been made to establish whether or not they have formed under the influence of the present climate.

Mulga (*Acacia aneura*) woodlands occur in the drier western portion of the red earth region, the trees being 15 to 25 ft. in height. Shrubs are unimportant. Eastwards, with increasing rainfall, mulga becomes less important, and the woodlands are gradually replaced by open forest 25 to 60 ft. tall (Beadle, 1948). There is frequently a tall shrub or small tree stratum and a well-developed herbaceous layer in the open forests.

Erosion of soils by wind is restricted to the drier, more sparsely vegetated, western portion of the red earth plains.

The solonetz regions

There are numerous, comparatively small, areas dominated by solonetzic soils, with minor occurrences of skeletal soils. The solonetzic soils have an A horizon, a few inches in depth, that varies from sand to sandy loam overlying, with a sharp boundary, a fine-textured to moderately fine-textured B horizon with a well-developed prismatic structure. Large amounts of carbonate appear at depths varying from 9 to 13 in. from the surface. There are variable amounts of gravel in the soils and on their surface and, in fact, many of them have a well-developed gravel pavement. The pavement may be over the entire surface, or may be irregularly developed due to the presence of a depression micro-relief similar to that in the stony tableland soil regions.

The associated vegetation is shrub-steppe dominated by low-growing shrubs; trees are absent except along drainage lines. When soil moisture is adequate, the ground between the shrubs is covered with herbaceous vegetation, but during droughty times it is bare and the soils without surface gravel pavements are then subject to erosion by wind.

The sand-ridge regions

There are a number of extensive sand-ridge areas with parallel longitudinal dunes. The flats separating the ridges consist either of deep sands, stony tableland soils, solonetzic soils, mallisols, or soils that are similar to grey-brown and red calcareous desert soils. The sand-ridges vary from 200 to 600 yds. apart and are normally 30 to 50 ft. high, although Madigan (1946) records ridges 100 ft. high in the Simspon Desert; their trend gradually changes from east-west in the southern sand-ridge areas to north-north-west—south-south-east in the Simpson Desert.

The association of the major sand-ridge areas with internal drainage basins (see Fig. 3) suggests that the ridges have formed as a result of the accumulation of coarse fractions derived through re-sorting, by wind, of lacustrine and alluvial sediments (cf. Gautier, 1935; Madigan, 1946).

In the southern sand-ridge areas tall shrubs form a discontinuous scrub on the ridges (Jessup, 1951) but this scrub is replaced farther north by open woodlands. These communities occur on both the slopes and crests of the ridges. In the Lake Eyre region and the Simpson

Desert (Crocker, 1946; Blake, 1938) scattered clumps of sandhill canegrass (*Zygochloa paradoxa*), a sclerophyllous grass, occur on the slopes of the ridges, the crests of which are bare.

Movement of sand under the influence of wind is evident in all of the sand-ridge areas, the greatest amount of re-sorting being in the dune crest. As would be expected, the ridges in the most arid (northern) areas show the greatest instability.

The skeletal soil regions

In north-western South Australia, south of Lake Cadibarrawirracanna, there is an area of pediment plains with skeletal soils. The plains consist of the exposed pallid zone of lateritic soils, of which relics are associated with scattered 'tent' hills that rise above the plains. The pallid zone material (somewhat silicified and non-calcareous kaolinite) is overlain by patches of very shallow (normally less than 4 in.) highly calcareous soil, in which the carbonate is obviously of extraneous origin. The area supports a very sparse and patchy shrub-steppe vegetation.

Skeletal soils are also associated with the Barrier, Willouran, and Denison Ranges, on which the principal vegetation is mulga (*Acacia aneura*) woodland.

The lateritic soil regions

As indicated above, there are scattered occurrences of lateritic residuals of minor extent in a number of the soil regions, but there are also areas in which plateaux or groups of 'tent' hills, with variously truncated lateritic soils, dominate the landscape. The truncated profiles normally consist entirely of pallid zone, but occasionally part of the mottled zone has survived. Silicified layers commonly occur within the pallid zone (Jessup, 1960). Deposits containing ferruginous and silicified materials derived through truncation of the laterites were laid down over the exposed mottled or pallid zones. The uppermost layer of these deposits has subsequently been silicified and there has sometimes been some silicification within them. The indurated (silcrete) capping is now overlain by either stony tableland soils, red earths, or highly calcareous soils, the parent materials of which must have had an extraneous origin.

The Nature of Contemporary Erosion and Deposition

In the section dealing with the soil regions brief descriptions of the dominant soils have been given. Truncated (eroded) profiles also occur; these can be traced laterally to sites where the entire profile is preserved and in this way the proposition that truncation has occurred can be substantiated.

In addition to the complete and truncated profiles there are sheets or mounds of materials overlying them in which there is no recognizable soil development (Plate II, Fig. 1). Instead, these superficial deposits have a fine horizontal or current-bedded lamination due to the presence of alternating layers of coarser and finer particles; in other words bedding exists in these materials which are considered to be newly-deposited

sediments. The materials in them are derived from the adjacent eroding soils, and the active agency involved in their deposition is wind, and in some cases, water.

Wind is the principal eroding agent in the south-eastern portion of the Australian arid zone (Ratcliffe, 1936, 1937). However, wind erosion only affects the soils in the more arid areas, that is, those receiving less than about 12 in. average annual rainfall. Elsewhere the soil surface is permanently protected by a well-developed vegetative cover.

The vegetation in these drier areas consists of woodland, shrub steppe, and occasionally scrub communities, but the shrubs and trees do not form a continuous cover. The soils are only completely covered after rains, when herbaceous plants appear. During droughts the soil surface is bare and subject to erosion. Although no form of agriculture is practised in the region, most of it is grazed by either sheep or beef cattle. The introduction of these grazing animals (and also of rabbits) has led to an increase in both the rate of wind erosion and the area that it affects.

The severity of wind erosion increases as the zone of maximum aridity (the Lake Eyre area) is approached, but the soils in any one locality are not all affected to the same extent, since susceptibility to erosion also depends upon the nature of the soils themselves (Chepil, 1954). For example, soils with a soft or incoherent surface such as those that are coarse-textured, or contain large amounts of amorphous carbonate, are more susceptible than soils with a firm coherent surface. Thus mallisols, soils that are similar to grey-brown and red calcareous desert soils and solonetzic soils are more severely eroded than red earths and grey and brown soils of heavy texture.

It is well known that wind removes the finer materials (clay, silt, and sand) from the surface of the eroding soil, leaving a residue of coarser materials such as grit, gravel, stones, and carbonate nodules. In the case of stony soils, erosion may ultimately be halted by the formation of stone or gravel pavements which completely cover the surface of the truncated soil.

Erosion of soils with incoherent surface horizons overlying firm coherent subsoils, such as solonetzic soils, is at first rapid, but following exposure of the subsoil is very much retarded in spite of the fact that the exposed soil is normally devoid of vegetation. Exposure of the fine-textured subsoil of solonetzic soils results in the formation of 'claypans' on which, because of the relatively impermeable nature of the sodium clay, water lies for a short time after rain.

Wind erosion of the longitudinal sand-ridges, even those with bare crests, does not result in the actual removal of sand from the ridge. The surface sand, particularly in the crest, is simply re-sorted. Most movement of sand occurs along the length of the ridge; side winds will displace a ridge laterally but only by toppling sand over the lee slope (Madigan, 1946).

In arid Australia plants play a major role in the trapping and retention of the wind-transported materials. The nature of the deposits that form is markedly influenced by the kind of vegetation on the landscape. In areas where the vegetation consists of sparse shrubs that branch at or

near the surface of the ground, the soil between the shrubs is eroded during droughty periods, and the wind-blown materials accumulate around the bushes to form mounds (Plate I, Fig. 1). The height of the mounds progressively increases as a result of both deposition on them and erosion of the inter-mound soil. Once this pattern of erosion and deposition is initiated the inter-mound areas become increasingly less hospitable for plant growth, while the mounds themselves provide a favourable habitat. Some species such as *Nitraria schoberi* and *Zygochloa paradoxa* continue to grow up through the mounds, and trap more and more wind-distributed material. Alternatively, the size of mounds may increase because of the continuous reproduction of shrubs on them. Mounds up to 6 ft. high and 30 ft. across are commonly formed where this pattern of erosion-deposition occurs (Plate I, Fig. 2); they are normally more or less rounded at the base, but may have an irregular shape.

In favourable sites in the landscape, the density of shrubs may be such that no wind erosion occurs between the bushes during droughty times. On the contrary, materials derived from adjacent areas may be trapped between the bushes, as well as around them.

Wind-distributed materials transported into an area with a continuous cover of herbaceous vegetation accumulate to form a shallow, uniform deposit.

It has been pointed out earlier that a characteristic feature of some solonetzic soil areas is the presence of a depression micro-relief. The inter-depression areas have stone-covered surfaces and are devoid of plants, while low-growing shrubs occur in the depressions. Wind-distributed materials, derived from any adjacent eroding areas and transported onto country with this type of micro-relief, accumulate around the margins of the depressions.

The deposits of wind-transported materials have certain well-defined characteristics; they show horizontal or current-bedding due to the presence of very thin depositional layers (usually $\frac{1}{16}$ to $\frac{1}{8}$ in. in thickness) consisting of sheets of alternating coarser and finer particles (Plate II, Fig. 1). This pattern of deposition may be due to variation in the size of particles transported by winds of different velocities. There is also a sharp and clearly-defined boundary between the wind-deposited layer and the underlying soil. The deposits vary considerably in depth; they form a discontinuous superficial layer mostly $\frac{1}{2}$ to 6 in. in thickness on most of the landscape but may be 6 ft. or more in depth in the crests of sand-ridges and where mounds are formed.

While the effects of water erosion and deposition are not as significant as in other deserts (see Discussion), rains of high intensity, causing rapid run-off, occur intermittently. Gravel and stones are moved down the hillslopes and are partly deposited along braided, very shallow channels that diverge from the foot of the hills. The position of the channels is continually changing. Finally the water spreads out on the adjacent plains where the remainder of the gravel is deposited. On both the foothill slopes and adjacent plains the water flows across the surface of *soils*, not bare rock pediments.

The distribution of the gravel deposited by these flashfloods is particularly interesting in areas where mounds of wind-distributed materials occur around bushes. The runnels flow and deposit their load of gravel between the mounds (Plate I, Fig. 1). The gravelly deposit may later be buried beneath wind-transported materials, in which case the alternation of water and wind deposition forms a system of stone-free mounds separated by wind-distributed deposits containing layers and lenses of gravel (Plate II, Fig. 1).

Discussion

The outstanding feature of the region is the presence of a great diversity of soils with widely differing characteristics. In spite of the aridity of the present environment there are lateritic soils with very deep zones of weathering, and red earths which, although often formed on calcareous parent materials, have a predominantly acidic reaction. At the other extreme there are soils that have undergone little leaching; these contain carbonate in the fine earth even at the surface. Furthermore, most of the soils have well-developed and deep profiles.

Deep soils with well-developed profiles rarely occur in other arid regions. The soils of the deserts of Syria (Muir, 1951; Reifenberg, 1952), northern Chile (Storie and Mathews, 1945), Cape Province of South Africa (Van der Merwe, 1941), central Iraq (Harris, 1958), the Kerman region of southern Persia (Beckett, 1958), the Sahara (Gautier, 1935), and the Turkana desert of Kenya (Hemming and Trapnell, 1957) show little or no profile differentiation and are generally shallow. In the Negev of Israel (Ravikovitch, Pines, and Dan, 1957) there are deep deposits of loess but there is no soil profile developed on them. Arid areas in which soils with differentiated profiles have been recorded are the Mojave desert of the United States (Brown and Drosdoff, 1940) and the alluvial plain of Iraq south of Baghdad (Buringh and Edelman, 1955).

Most of the soils in arid Australia have clayey subsoils; some consist of clay throughout the profile. Soils with high clay contents are apparently not widespread in the arid regions mentioned above; many of the deserts have very little or no clay in their soils, although alluvial and wind-transported deposits may contain fine fractions. This is well illustrated in the Turkana desert of Kenya (Hemming and Trapnell, 1957) which consists of areas of consolidated and unstable dunes, sand sheets and gravelly rock pediments; there are also areas of riverine alluvium and flashflood deposits but these do not have soils developed on them. Similarly the Sahara consists of sand-ridges, rock and gravel plains from which the fine fractions have been removed by wind, and rocky hills (Gautier, 1935).

Both wind and water erosion are apparently less severe in the arid regions of Australia than in most parts of the above-mentioned deserts, where there are very large areas of recently-deposited sediments laid down by wind, riverine, and sheetflood activity. An outstanding feature of these arid regions is the sparseness of the vegetation, the natural density of which has been drastically reduced as a result of long-continued and excessive grazing, nomadic cultivation and cutting of

plants for fuel. The Australian arid zone has had a brief history of utilization, and has a comparatively well-developed perennial vegetative cover.

Gautier (1935) states that the intensity of water erosion in the Sahara 'is out of all proportion to the amount of water involved'; similar statements are made with respect to the Gobi desert of Mongolia (Berkey and Morris, 1927) and other arid regions. Intense erosion is not only attributed to the sparseness of the vegetation and rains of high intensity, but also to the general absence or shallow nature of the soil cover, that is, to the occurrence of stony hills and mountains and bare rock pediments (Hemming and Trapnell, 1957).

Although rains of high intensity do occur in the Australian arid region, water erosion and deposition are less important because of the better-developed nature of the vegetative cover and the absence of extensive areas of bare rock pediments, hills, and mountains. However, in hilly areas where the perennial vegetation has been destroyed through overgrazing there may be severe water erosion leading to gully formation.

Whereas in most arid regions there are extensive areas of recently-formed sediments resting directly upon rocks, in arid Australia the recent deposits (principally of wind-distributed origin) form a superficial layer underlain by developed soils. Other areas in which recently-deposited sediments overlie developed soils are south of Baghdad in Iraq (Buringh and Edelman, 1955) and the Mojave desert of the United States (Brown and Drosdoff, 1940).

Acknowledgements

The writer is indebted to Mr. B. E. Butler, Division of Soils, C.S.I.R.O. for valuable suggestions during the writing of this paper. Diagrams and maps were drawn by Mr. J. M. Kalmar (C.S.I.R.O.) who also assisted with some of the field work.

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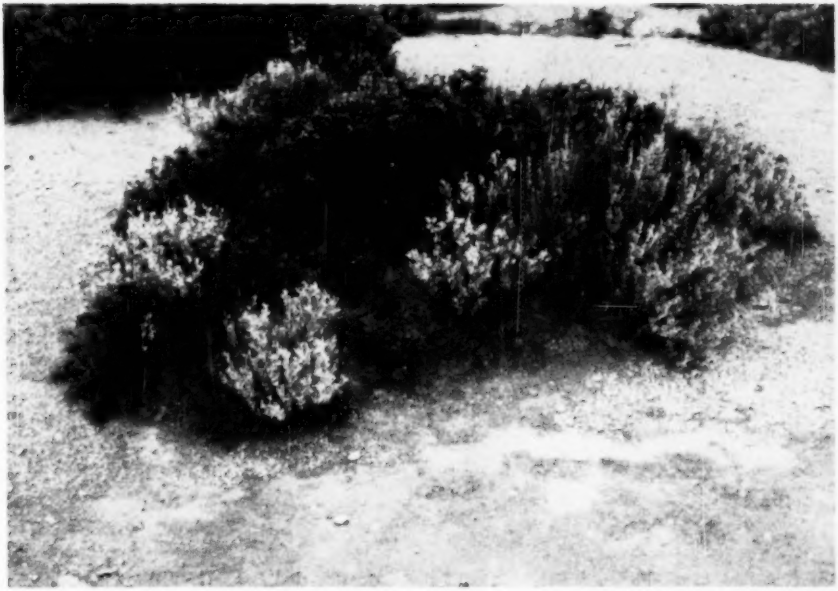

FIG. 1. Mound of sand trapped around shrubs (*Nitraria schoberi* and *Atriplex vesicaria*). The gravel on the surface of the inter-mound areas has been deposited by flashfloods

FIG. 2. Mounds of wind-transported materials, 6 ft. in height. Increase in the size of these mounds has been due to the continuous reproduction of shrubs (particularly *Kochia pyramidata*) on them. Note that bare portions of the mounds have been eroded by water

R. W. JESSUP—PLATE I

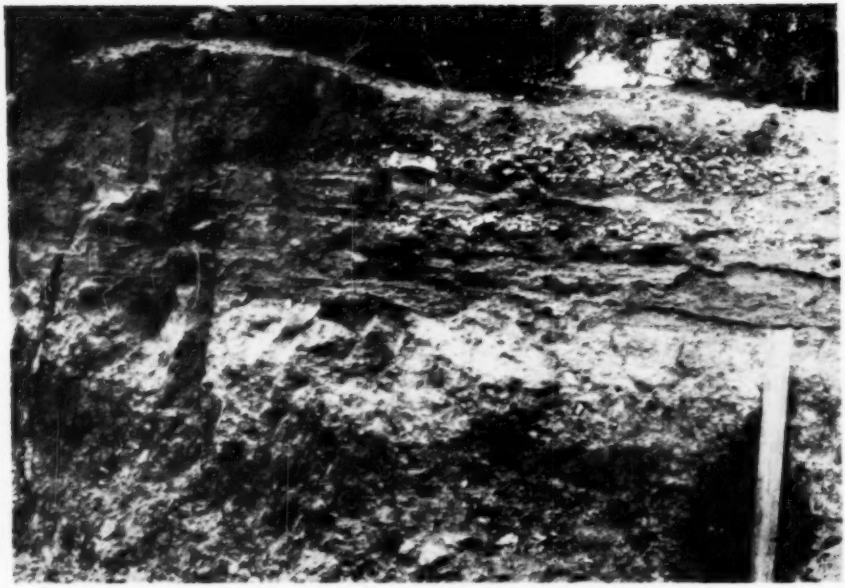

FIG. 1. Photograph illustrating the formation of a stone-free mound of wind-distributed material with an adjoining deposit of wind-distributed material containing layers of gravel due to flashflood deposition. Note the horizontal bedding in the wind-blown materials, and the sharp boundary between these and the underlying soil which is a solonetz (the boundary is just below the top of the ruler)

R. W. JESSUP—PLATE II

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THE LATERITIC SOILS OF THE SOUTH-EASTERN PORTION OF THE AUSTRALIAN ARID ZONE

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Summary

Remnants occur in arid Australia of a formerly extensive land surface on which deep lateritic soils were developed. The lateritic profile, which contained silicified layers in the upper portion of the pallid zone, was subsequently truncated and water-transported deposits containing lateritic detritus were laid down over the exposed mottled or pallid zones. Silicification of the upper portions of these deposits resulted in the formation of surface silcretes (the duricrust).

The silcrete capping on the lateritic plateaux is overlain by either younger soils formed on deposits of wind-transported materials, or by deposits of wind-blown gypsite. Gypsum, leached from the latter, has accumulated in the mottled and pallid zones of the lateritic profile.

Introduction

THE presence of laterite in the arid interior of Australia has long been recognized (see Prescott and Pendleton, 1952). Woolnough (1927) described a widespread indurated surface layer, either highly ferruginous or siliceous, that capped residuals of a formerly extensive peneplain and proposed the term duricrust for these cappings. Whitehouse (1940) suggested that the duricrust resulted from exposure, through erosion, of indurated zones that had formed within lateritic soil profiles, and that there were two periods of laterite formation in western Queensland.

During the present investigation lateritic soils in two extensive and representative areas in the south-eastern portion of the Australian arid zone were studied; the location of these two areas is discussed in an earlier paper (Jessup, 1960).

The Lateritic Residuals and the Materials exposed in their Scarps

The landscape of the region consists principally of vast plains that range from a few feet below sea-level in the vicinity of Lake Eyre to a maximum of about 500 ft. above sea-level (Jessup, 1960). Rising abruptly above the plains to heights commonly varying from 100 to 300 ft. are remnants of a formerly widespread land surface.[1] These remnants form plateaux or, where of small extent, more or less flat-topped ('tent') hills (Plate I, Fig. 1). The plateaux and 'tent' hills, as can be seen from their scarps, consist of a great thickness of the pallid zone of a lateritic soil.

A group of small lateritic plateaux and 'tent' hills forms the Stuart–Painted Range in South Australia and the McGregor Range in Queensland. However, the most extensive plateaux occur in the Grey Range

[1] There are also remnants of an older land surface.

in Queensland; the surface of these plateaux is markedly undulating, differences in relief amounting to 100 ft. or so in half a mile (Plate I, Fig. 2). Furthermore, the plateaux slope upwards towards their margins where the highest elevations are found and it is evident that the broad valleys separating adjacent plateaux have been eroded in the highest parts of the original land surface.

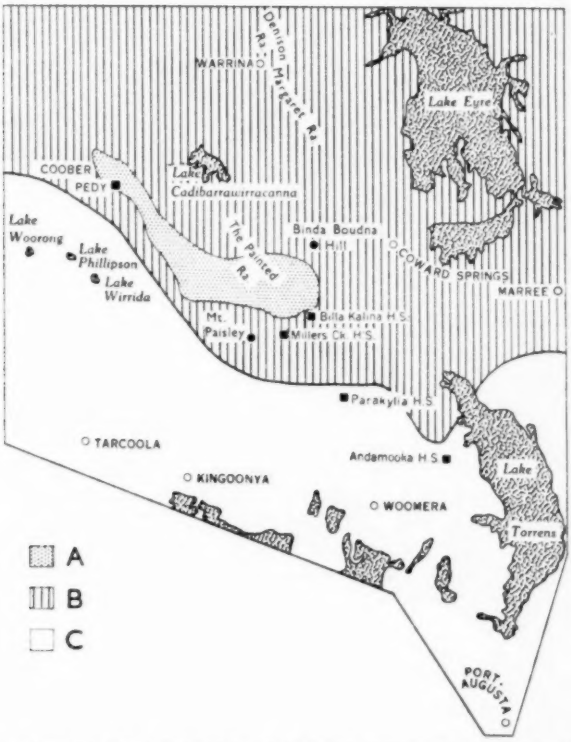

FIG. 1. Showing the distribution of plateau remnants with lateritic soils (South Australian area). Zone A, major occurrence. Zone B, scattered residuals. Zone C, lateritic land surface destroyed by erosion.

The lateritic land surface was formerly very extensive; there are small isolated remnants throughout the greater part of the areas studied (Figs. 1 and 2).

The plateaux are capped by a layer of quartzite which varies from 2 to 15 ft. in thickness. Sometimes there are irregular patches of soft sandstone or grit within the quartzite.

This hard surface layer is underlain by deposits, 2 to 18 ft. in thickness, containing variable amounts of porcellanite and quartzite gravel and stones. The quartzite stones may be rounded or angular while the

porcellanite fragments are always angular. In many sites the size of the stones is extremely variable, indicating an absence of sorting. The stones occur in a matrix of either kaolinitic clay, sand, or highly ferruginous material. Thin sections of the ferruginous matrix have been prepared; they show that it consists of a haematitic groundmass containing quartz grains, clay (kaolinite), and other inclusions and that there is some crystalline haematite or goethite in cracks.

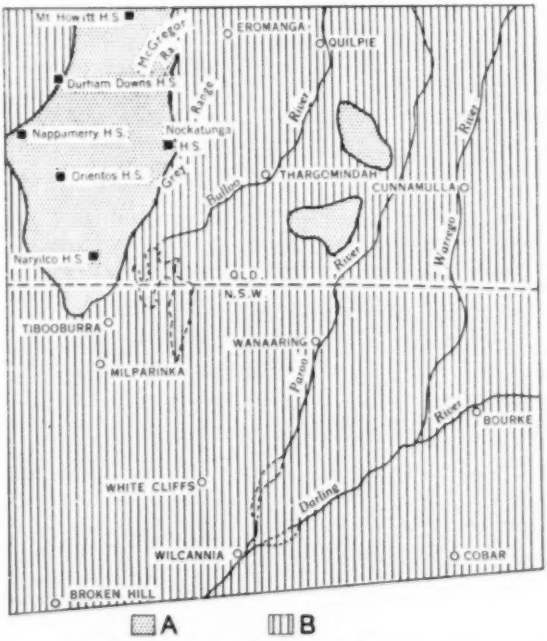

FIG. 2. Showing the distribution of plateau remnants with lateritic soils (New South Wales—Queensland area). Zone A, major occurrence. Zone B, scattered residuals.

In other scarps the quartzite capping is underlain by varying depths (15 to 50 ft.) of soft sandstones together with some grits.

The sandy or stony deposits may contain silicified layers, seams, or patches. Thus quartzite occurs within sandstones and grits, conglomeratic quartzite within deposits consisting of quartzite stones in a sandy matrix, and red-coloured jasper within highly ferruginous deposits. Silicification has been quite variable; thus there are all gradations, for example, from soft sandstone to hard quartzite.

These deposits usually overlie a great depth of white clay or white clays and soft sandstones. The pallid material extends to the bottom of the scarps; depths varying from 60 to over 200 ft. may be observed.

X-ray analyses show that the clay is kaolinite. In some localities, such as Coober Pedy, pockets of alunite are common in the white kaolinite.

Towards the top of this deep, pallid material there are usually silicified layers. Within the kaolinite there are layers of porcellanite, and within the sandstones layers of quartzite. The intensity of silicification has varied with the result that all gradations between these highly indurated materials and unaltered kaolinite or soft sandstone may be found. The upper 15 to 50 ft. of the pallid material may have silicified materials in it.

Towards the lower portions of the scarps the pallid material frequently

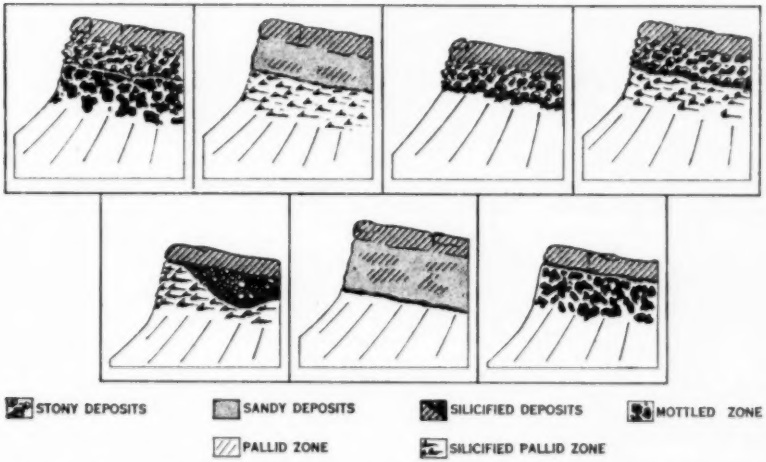

FIG. 3. Diagram showing the different sequences exposed in scarps of the lateritic plateaux.

contains large yellow patches within which there may be seams of ironstone. These seams have soft earthy limonite and haematite cores enclosed within and containing hard ferruginous concretionary layers frequently coated with pyrolusite.

Some plateau scarps have variable thicknesses (10 to 30 ft.) of red and white mottled kaolinite or kaolinite and soft sandstone overlying the pallid material (Fig. 3).

The whole sequence described above is non-calcareous, but cracks filled with crystalline gypsum are common in the pallid and mottled materials in the Stuart, Painted, Grey, and McGregor Ranges and adjacent areas. Elsewhere seams of gypsum do not occur.

Throughout the greater part of the region the pallid materials are underlain by rocks of Cretaceous age (Jack, 1930; Kenny, 1934; Bryan, 1946) consisting of shales, mudstones, and sandstones with some thin limestone beds. X-ray analyses of the shales and mudstones show that they contain both kaolinite and illite. There are no quartzite beds in these Cretaceous deposits.

Conclusions

The land surface of which the plateaux are remnants had lateritic soils developed on it. This is indicated by the great depth of weathering and by the fact that the clay minerals in the parent rocks have been kaolinized. The red and white mottled material is the mottled zone, and the great depth of white material is the pallid zone, of the lateritic profile. There was also a ferruginous zone, but this has been removed by erosion (see below).

Well-developed lateritic profiles form in hot moist climates (D'Hoore, 1954). Under these climatic conditions large quantities of alumino-silicates are decomposed with the liberation of silica and sesquioxides. Some of the silica released during lateritization can apparently be deposited within the lateritic profile (Mohr, 1933) and the silicified layers in the pallid zone of the laterites of arid Australia apparently formed in this way. The intensity of silicification was variable with the result that there are all gradations from unsilicified kaolinite to porcellanite and from sands and grits to quartzite. The term silcrete is applied to porcellanite and quartzite resulting from secondary silicification (Williamson, 1957).

From the sequence of materials exposed in the plateau scarps, it is evident that, following their formation, the laterites were variously truncated by erosion, sometimes to the mottled zone but more frequently to the pallid zone; the silicified layers in the latter would have protected the underlying soft materials. Deposits containing lateritic detritus were laid down over the truncated profiles. These deposits occur in even the highest parts of the plateaux, that is, around their margins; this indicates that laterites also occurred on more elevated portions of the original land surface than those that have survived erosion. The fragments of silcrete (porcellanite and quartzite) in the deposits were derived from the silicified layers within the pallid zone of the lateritic profile. The materials in the highly ferruginous deposits were principally derived from the ferruginous zone of the laterites, but the presence of silcrete fragments indicates contamination with materials from other horizons (cf. Frankel and Kent, 1937).

The quartzite capping on, and the silicified layers within, the deposits of lateritic detritus result from a later silicification. There are all gradations from unsilicified to strongly silicified materials. As the deposits varied considerably in their nature, a variety of silcretes resulted from their silicification. Thus intense silicification of sands and grits produced a quartzitic silcrete, the silicification of deposits with fragments of silcrete in a sandy matrix gave rise to a conglomeratic silcrete (cf. Frankel, 1952) and the silicification of highly ferruginous deposits formed a red-coloured jasper.

The source of the silica involved in this silicification has not been established. It may have been derived through re-solution of silica contained in the silicified materials in the lateritic profile, since thin sections reveal that solution and subsequent crystallization of silica from silcrete does occur (Williamson, 1957). Silica may also have been derived from rocks in the higher sites (later destroyed by erosion) in the original land

surface, either where laterites did not occur or where unweathered rocks were exposed during erosion of the laterites.

There remains to be considered the origin of the alunite and ferruginous seams in the pallid zone, and of the gypsum seams in the mottled and pallid zones. Grains, nodules, and lenses of pyrite occur in the unweathered Cretaceous rocks. The occurrence of ferruginous seams with coatings of pyrolusite, and of alunite, in the lateritic profile is probably related to the presence of this pyrite in the parent materials. Baas-Becking (unpublished data) has shown that oxidation of pyrite can occur in waterlogged soils; its oxidation gives rise to acid sulphate ion which reacts with clay minerals to form alunite (Butler and Gale, 1912). Formation of the alunite would have taken place prior to complete kaolinization of the clay minerals, since kaolin does not contain the potassium necessary for alunite formation. Presumably, therefore, the alunite formed during the earlier stages of weathering.

Simpson (1923) investigated the formation of a similar assemblage of minerals in the pallid zone of lateritic soils derived from pyrite-bearing rocks containing limestone beds. Concretions and seams of iron oxide result from the oxidation of ferrous carbonate formed by neutralization, with lime, of ferrous sulphate which was derived from the pyrite oxidation. Gypsum is also formed during these reactions. Pyrolusite owes its origin to small quantities of manganese present in the limestone beds. The manganese reacts with acid sulphate ion from the pyrite oxidation to form manganese sulphate which is neutralized by lime. Gypsum is also formed. Pyrolusite results from oxidation of the manganese carbonate.

These end products (iron oxide, manganese oxide, and gypsum) may be produced by alternative mechanisms, but the initial reactants and products are the same in all cases.

Because of its solubility the gypsum formed during these reactions would have been removed during lateritization.

The surfaces and scarps of the lateritic plateaux are now overlain by younger soils—red earths, stony tableland soils, or calcareous soils (Jessup, 1960)—or highly gypseous deposits. The composition of these soils contrasts with that of the underlying materials and it is clear that the parent materials on which the soils developed had an extraneous origin. Thus, neither the pallid zone of the lateritic profile nor silcrete could have provided the parent material for the development of the calcareous soils that overlie them in some areas. Other anomalies are the presence of non-argillaceous rocks such as quartzitic silcrete and sandstones beneath fine-textured stony tableland soils and red earths. The gypsite deposits, too, occur on mottled and pallid zones of the lateritic profile and the silcrete capping on the residuals, as well as a variety of other non-gypseous materials.

These soils and deposits are not confined to the lateritic plateaux but occur between them on remnants of another land surface and also on the extensive youngest land surface. As they are found over the entire landscape, irrespective of relief, it is concluded that the parent materials of the soils and the materials in the gypsum deposit were transported and

deposited by wind. The sources of these wind-transported materials and the genesis of the soils formed on them will be discussed in later papers.

It has already been pointed out that there are seams of crystalline gypsum in the mottled and pallid zones of the laterite in some localities. As these seams only occur where there are gypsite deposits on the slopes of the lateritic residuals, it seems reasonable to assume that the gypsum in the seams was leached from these deposits. Sometimes, as at Coober Pedy, horizontal seams of crystalline (satinspar) gypsum as much as 6 in. in thickness are found in the pallid zone. The cavities in which this gypsum was precipitated may have been formed by destruction of thin limestone beds during lateritization. The seams of gypsum are not continuous in the horizontal plane; this may be due to the fact that removal of the limestone beds was accompanied by irregular subsidence of the overlying materials.

Discussion

The interpretation of the sequence of materials in the scarps of the lateritic plateaux presented in this paper differs somewhat from that of previous workers. Evidence of only one period of laterite formation has been found whereas Whitehouse (1940) suggested that the presence of cappings of lateritic ferruginous zone on isolated, small land surface residuals at two levels in western Queensland indicated two periods of laterite formation. However, investigations in the Grey Range, where extensive lateritic residuals occur, reveal that the landscape on which the laterites developed had considerable relief and that dissection has left isolated remnants of different height. Whitehouse (1940) has recorded the formation of a second lateritic profile on deposits containing lateritic detritus; no corresponding evidence has been found in the areas investigated.

The origin of the siliceous duricrust has been the subject of considerable controversy. Woolnough (1927) suggested that it formed at the surface of a peneplain as a result of the upward movement of capillary waters containing silica in solution, during a former humid period. Whitehouse (1940) stated that the duricrust resulted from exposure, through erosion, of the silicified zone of lateritic profiles. Jackson (1957) proposed that these cappings were a product of the present arid environment.

In the areas investigated the duricrust is not the exposed silicified zone of the lateritic profile; it formed as a result of the silicification of water-transported deposits laid down over the exposed pallid or mottled zones. There is only one duricrusted land surface as suggested by Woolnough (1927). The presence of duricrust on isolated plateau remnants of different height, as recorded by Stephens (1958), is not indicative of more than one duricrusted land surface, but results from dissection of a single land surface with considerable relief.

The formation of the duricrust cannot be attributed to the present arid environment as suggested by Jackson (1957); its relic nature is indicated by its presence on the old land surface residuals and its absence from the younger land surface. The whole landscape, including the silcrete-capped plateaux, has been buried beneath wind-transported

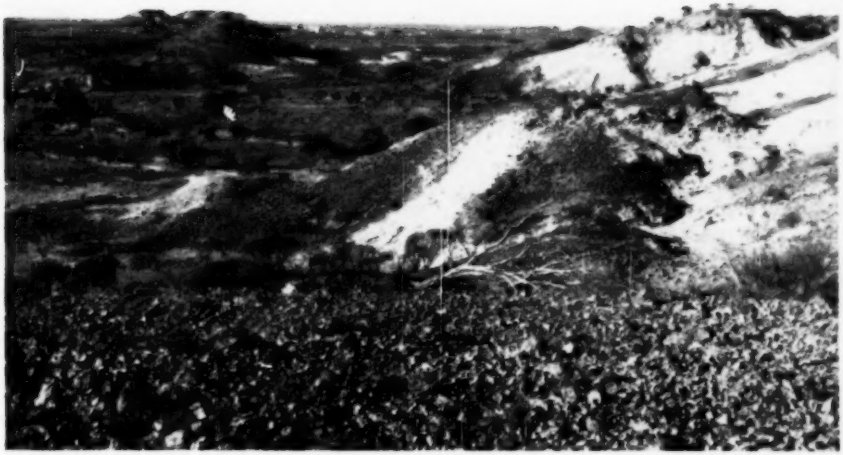

FIG. 1. Typical plateau remnants of the lateritized land surface, Painted Range. Note the great depth of pallid zone exposed in the scarps; the stones are fragments derived from the surface silcrete layer

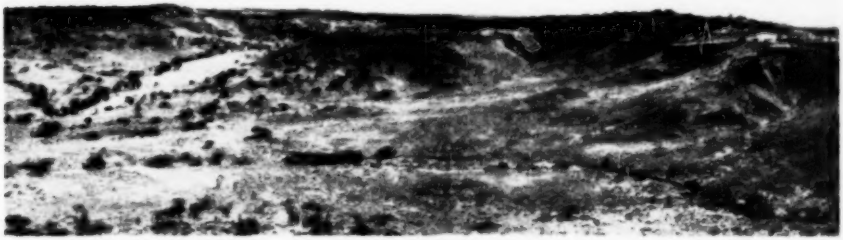

FIG. 2. The southern margin of the lateritic plateau, Grey Range near Tibooburra. Note that the surface of the plateau has considerable relief

R. W. JESSUP—PLATE I

materials. There are several layers of these deposits, most of which have had soils formed on them. As will be shown in later papers, the deposits and soils are of Quaternary age. None of these younger soils have silicified layers; this seems to indicate that silicification is not a contemporary, and was not even a recent, process.

No very satisfactory dating of either the formation of the lateritic soil or of the post-laterite silicification has been possible. Whitehouse (1940) suggested a Pliocene age for the formation of the laterites of western Queensland. Woolnough (1927) believed that the duricrust formed during the Miocene.

Acknowledgements

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SALINE SOILS IN THE KIRKUK PLAIN, NORTHERN IRAQ

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Summary

The Kirkuk Plain has undergone partial salinization, followed by weak leaching. The areas irrigated in the past are the worst affected. Quality and quantity of irrigation water are most important factors in controlling the degree of salinization, while minor factors include deep gullies and the presence of a gypsum bed near the surface. The salts originate from the Fars Beds and the gypseous alluvium. Saline soils were encountered in areas with water tables much deeper than 2 m.

Introduction

SMITH (1957) has observed that the steppe soils in Central Iraq have reverted to arid grazing following widespread abandonment of irrigation over 600 years ago. The soils are developed on highly calcareous alluvium, the carbonate being derived from limestones of the Tigris basin. Gross salinity can be detected in the field over large parts of the alluvial plain; the soil surface may be bare because the high salt content inhibits the growth of all but a few salt-tolerant plants. Analysis of water-soluble extracts of a great number of soils shows that sodium chloride is the main constituent. Gypsum, which is only moderately soluble, is present in many profiles, especially those of fine texture. These salts are derived from the oceanic salts in the marine sediments which occupy much of the Tigris drainage basin and which include widespread beds of gypsum. The present observations relate to the Kirkuk Plain which lies among the outermost folds of the Persian mountains about 150 miles north of Baghdad. The area has a hot, dry summer and a cool wet winter. The mean annual rainfall varies from 300 to 400 mm./year, increasing north-eastwards. Further data are given in *Climatological Means for Iraq* published by the Ministry of Communications and Works (1950 and 1954). Parts of the Kirkuk Plain were irrigated in the past as is evident from traces of the former canals, and parts are now irrigated. Until recently drains were not used, a fact which may help to explain why large areas of the plain have become saline. A study has been made of the soil salinity in relation to surface topography and to depth of the water table.

Physiography

The area lies amongst the outermost folds of the Persian mountains between the Jebel Hamrin and the main folds of the Foothill Zone (Fig. 1). There is a gentle south-westerly slope away from the latter. The plains themselves are incompletely divided into three areas by the southern continuation of the Jebel Batawa and the northern continuation of the Jebel Tauq. The Kirkuk structure forms the eastern boundary of the area.

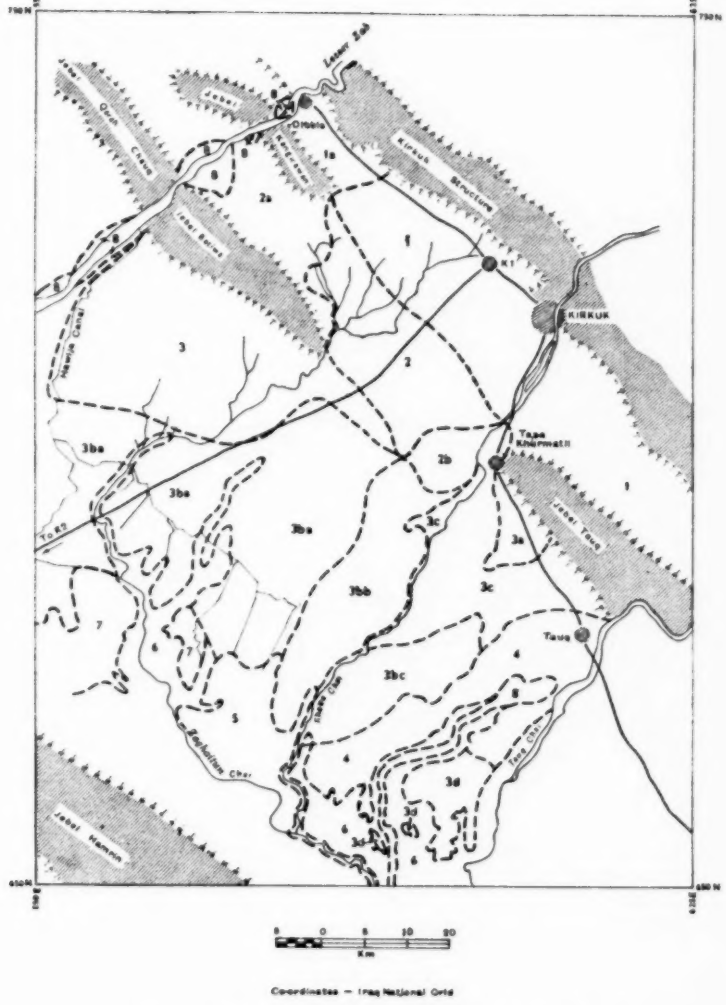

FIG. 1. Physiographic divisions of the Kirkuk Plain.

1. Kirkuk Plain
1a. Gully erosion of the Kirkuk Plain
2. Yachi Plain
2a. Gully erosion of the Yachi Plain
2b. Irrigation deposits on the Yachi Plain
3. Hawija Plain
3a. Gully erosion of the Hawija Plain
3ba. Former Lesser Zab Canals
3bb. Former Khasa Chai Canals
3bc. Former Kaur Darreh Canals
3c. Bushairiya Plain
3d. Gaida Plain
4. Tauq alluvial fan
5. South-western gypsum mounds
6. Zaghaitun Chai gully erosion
7. Undulating gypsum and gravel hills
8. River terraces

The Lesser Zab river forming the northern boundary of the area is considerably entrenched into the plains. It is rapidly eroding its bed and has evidently been able to maintain its ancient torrential course across the opposing ridges, an example of antecedent drainage. Formerly, water from the Lesser Zab river was led across the wide area marked 3ba on Fig. 1 and the lines of the old canals are marked by deposits thrown down where the irrigation water lost speed. There is a fan-like area of deposits in the area 2b which is situated near the offtake of the former Khasa Chai canals serving the area 3bb. No doubt much alluvial material was thus led on to the area and deposited there by a human adaptation of the normal geological processes of erosion and deposition. On the other hand the plains are being eroded by an extensive system of deeply entrenched gullies represented in Fig. 2. This appears to be the result of tilting of the plain with some minor folding subsequent to the previous period of extensive irrigation. The Tauq Chai, rising in the foothills of the Persian Mountains forms the south-eastern boundary of the area now described, while the Zaghaitun Chai and the Hawija canal form the western boundary. Lateral corrosion is subordinate to down-cutting except near the Zaghaitun Chai. Gully erosion leading into this channel is destroying the Gaida plain (marked 3d in Fig. 1).

Soils

The soils of the area are divisible into three groups, viz. those overlying gypseous alluvium at less than 1½ m., those formed on deep, natural, non-gypseous alluvium, and those formed on old irrigation deposits.

The gypseous alluvium appears to underlie most of the plains at varying depths. It lies at shallow depth in various parts of the area, notably between the Jebel Batawa and the Hawija canal. The quantity of gypsum varies up to 60 per cent., but is normally only mapped where more than 10 per cent. is found.

The other soils are typical of the non-gypseous Mesopotamian alluvium in other parts of Iraq (Smith and Robertson, 1956; Harris, 1958). The natural alluvium differs from the irrigation deposits by being far more uniform with no sandy loams or sandy horizons at depth.

The soils contain varying percentages of alkaline-earth carbonates, usually in the 20–30 per cent. range. Negligible profile development has taken place.

The irrigation deposits occur on the lower parts of the plain, but cut across the contours. Characteristic 'gilgai' soils are abundant on areas of fine grained material between the digitate irrigation deposits of coarse grain (Harris, 1958). This is a manifestation of the poorer structural condition in these soils as compared with the natural alluvium. Gilgai are rare in the area of natural soils and their geographical limit occurs between the Jebel Batawa and the Jebel Tauq.

The evolution of the landscape may be considered in relation to the formation of the gypsum bed now widely present under a varying thickness of alluvial fan, aeolian, and riverine material. According to many authorities (e.g. Voûte, 1957), the presence of a considerable thickness

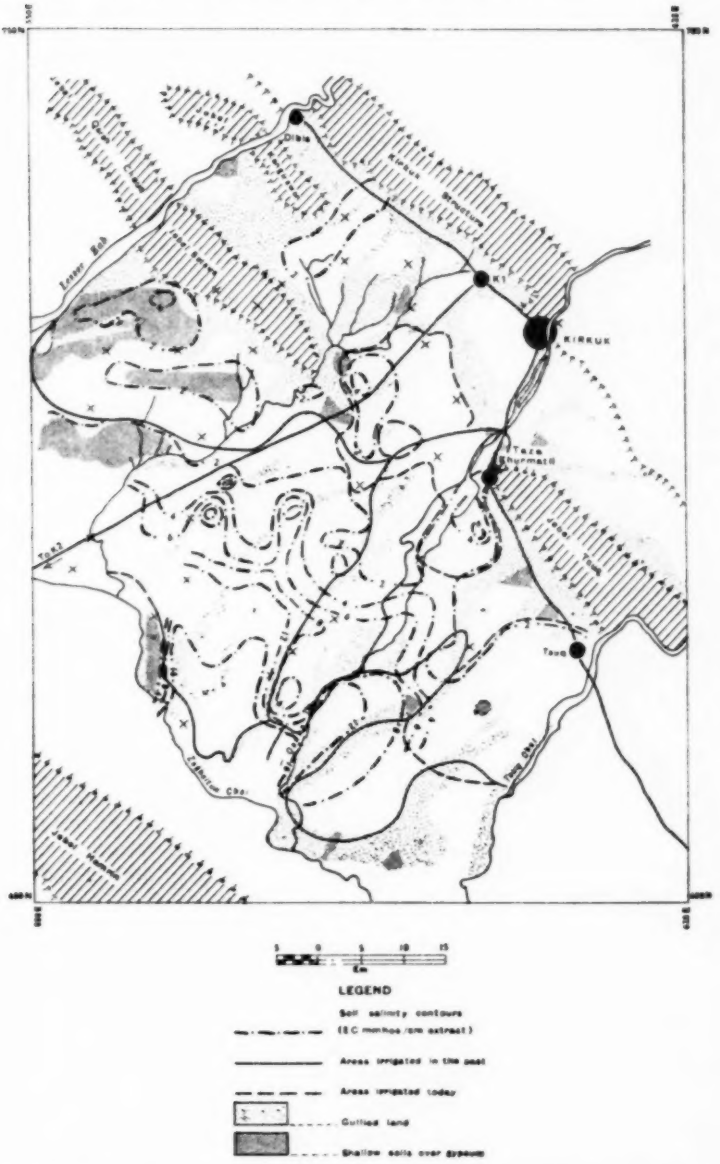

FIG. 2. Salinity distribution in the top 2 m. of the gypsum-free horizons of the Kirkuk Plain.

of gypseous alluvium suggests a stable surface with regular inflow of seepage water to maintain a water table sufficiently near the surface to permit loss of water by evaporation or other processes leading to progressive separation of the somewhat sparingly soluble gypsum. Other salts must have separated out locally at the same time, but these were no doubt more readily washed away under climatic conditions not widely different from those now affecting this region. This supposedly more or less stable situation has been interrupted by tilting towards the south-west and the development of a ramifying and deeply entrenched system of gullies, many of which lead into the Zaghaitun Chai.

Factors affecting Salt Distribution in the Area

The area includes non-saline and saline soils and, as shown in Fig. 2, there is some regularity in their distribution. The numerals on the figure relate to electrical conductivities of extracts made of soils to a depth of 2 m. excluding highly gypseous horizons. The distribution of soil salinity has been considered in relation to the following factors:

1. Whether the place has been irrigated.
2. The salinity of the irrigation water in irrigated areas.
3. Areas where the distribution of gypsum in the profile is important.
4. Nearness to marked gully systems.
5. Depth to the water table.
6. Salinity of the water table.

1. *Areas of irrigation—past and present*

Generally speaking, the areas irrigated in the past have higher salinities than the surrounding areas. In Fig. 2 the marked boundary formed by the closely concordant 4- and 6-mmhos/cm. lines probably delimits the former high-water-table areas. It is in such areas that the maximum salt accumulation would have occurred. From the studies of numerous present-day areas of irrigation it is well known that a slight decrease in depth to the water in a high-water-table area results in a considerable increase in salinity. Since the area is under leaching conditions today, the present salinity is probably appreciably less than that which has existed in the past.

The natural soils generally have a salinity of less than 4 mmhos/cm. except in one locality surrounded on three sides by areas of past irrigation and in two areas of present-day irrigation. In the first case, the soil was probably salinized by high water tables induced by the nearby irrigation.

That all irrigated lands are not saline is shown by the present-day and past area of irrigation of the Tauq Chai. This area shows only slight salinity (2–4 mmhos/cm.) in spite of a considerable period of use. Thus some other factors related to the application of irrigation water must be considered in order to account for these anomalies.

2. *The quality of the irrigation water*

The analyses of river water shown in Table 1 refer to water samples collected at all seasons of the year and are thought to be a fair sample.

The other sources were sampled in the spring when the salinity might be expected to be at a minimum corresponding to the height of the wet season. The waters are of good quality, being of low salt content and having a low proportion of sodium, though the river waters are far better than the groundwater. Much more saline waters are used successfully elsewhere so that if any adverse effect is noted here it is likely to be due to the method of use rather than to any defect in the waters.

Three small areas are irrigated today. One lies near Tauq and uses the winter flow of the Tauq Chai. A second is based on the Kaur Darreh which is a gully system coming through the northern end of the Jebel Tauq. It has a small flow in spring and summer, based on drainage water from the highest plain. This irrigates a limited area near Taza Khurmatli. The third area lying south-east of Jebel Batawa is based on 'Kareze' water, that is, underground water withdrawn from aquifers between the northern continuation of Jebel Tauq and Kirkuk town. A small area of increased salinity lies on the edge of this irrigated area at the foot of the slope against the southern continuation of the Jebel Batawa where the irrigation ditches finish in an average year. Similarly there is a salty patch south of Taza Khurmatli on the edge of the Kaur Darreh irrigation. By contrast the area at present irrigated from the river Tauq is non-saline. Analyses given in Table 1 show the Tauq Chai water to be less saline than the 'Kareze' water, but since all are of excellent quality, this difference can hardly be decisive. The more salts an irrigation water may contain, the greater the leaching requirement. It is likely that when the 'Kareze' water is used, the amount applied is insufficient to carry salts away in drainage water.

The major problem in the present-day irrigation systems is the shortage of irrigation water which results in the minimum application of water necessary to grow winter crops in most of the area. In summer virtually no irrigation takes place owing to the almost complete drying-up of the streams. The limited water available is chiefly used to keep the human and livestock populations going except for a small area at Taza Khurmatli.

In the past, this situation did not apply to the whole area. The large area watered from the Lesser Zab could be watered in summer since that river has a fairly large summer flow. Also, water applications during the winter could be greater. The areas of highest salinity do not appear to correspond to any one of the areas irrigated in the past.

The areas formerly irrigated by the Khasa Chai and Tauq Chai are outstanding by their lower salinities compared with the neighbouring areas. Analyses given in Table 1 show that both waters are of excellent quality. The soils are readily permeable, and in spite of the lack of drains the low salinity of the soil agrees quite well with this analysis, assuming that the present small area having a higher salinity than 4 mmhos/cm. is due to a high water table. The Kaur Darreh area of ancient irrigation deposits and half the area of soils formerly irrigated by the Lesser Zab river show marked salinity. A large part of this is probably due to the former area of high water table indicated by the 4–6 mmhos/cm. average-salinity lines. In the case of the Lesser Zab

TABLE I

Composition of Water from Various Environments in the Kirkuk Area

Type of source	*Site*	*Anions (m.e./litre)*						*Cations (m.e./litre)*				*T.D.S. p.p.m.*
		Cl'	SO_4''	CO_3''	HCO_3'	NO_3'	*Total*	Ca^{++}	Mg^{++}	Na^{+}	*Total*	
Lesser Zab R.	Dibbis	0·4–1·1	0·3–0·5	2·9–3·3	..	..	3·6–4·9	2·3–3·0	0·9–1·2	0·1–0·7	3·6–4·9	193–268
Khasa Chai	Kirkuk	0·3–0·5	1·3–1·4	3·6–5·3	..	..	5·3–7·1	2·5–2·7	1·9–2·6	0·9–1·6	5·3–6·9	300–360
Tauq Chai	Tauq	0·6–1·1	0·9–2·9	3·0–3·8	..	..	5·7–7·8	3·2–4·4	1·0–2·7	0·3–1·7	5·7–7·6	350–450
Sulphur Spring	Baba Gurga	0·9	32·7	3·1	..	..	36·7	33·0	3·5	1·7	38·2	2500
		0·4	2·0	3·6	..	..	6·0	4·2	1·4	0·4	6·0	360
Kareze Water	W7	0·9	5·4	..	5·2	0·6	12·1	3·6	6·4	3·0	13·0	835
	W21	0·9	8·8	..	4·7	0·3	14·7	5·2	5·6	3·6	14·4	1100

canals, the considerable area with high salinities is probably the result of a more copious application of irrigation water producing a larger area of high water table which would permit accumulation of salts in the soil. The Kaur Darreh area probably suffered from a small flow of more saline drainage water used over a wide area in too small a quantity to leach out all the salts introduced to the soil.

3. *Areas of shallow gypsum*

The solubility of gypsum in the soil paste is sufficient to affect the electrical conductivity. Any small quantities of water-soluble impurities in the gypsum bed will also considerably increase the conductivity results. Many of the soil profiles include horizons containing gypsum of a fine-textured, earthy form. If the gypsum content is plotted against electrical conductivity, a marked lower limit of conductivity at 1·5 mmhos/cm. paste (or 2·5 mmhos/cm. extract) is obtained at all gypsum contents above about 1 per cent. Since the normal salinity for non-gypseous horizons ranged down to 0·4 mmhos/cm. paste, it would seem that electrical conductivity is considerably modified by the presence of small quantities of gypsum. Water-extract analyses of the gypsum bed (Table 2) suggest the presence of both sodium and magnesium sulphates. The increase in abundance of these more soluble salts with depth below the top of the gypsum bed is also worth noting.

TABLE 2

Cation Distribution in the Gypsum Bed in Pit R12, Kirkuk Plain

Depth (cm.)	*% of total cations*		
	Ca	Mg	Na
70–150	73	19	8
150–200	57	31	12
250–300	45	38	17
350–400	36	38	26
440–470	35	35	30

If movement of the gypsum or the other sulphates occurs, this may be apparent in the salinity distribution. Although horizons containing more than 1 per cent. gypsum were ignored in producing the salinity-distribution map (Fig. 2), a tendency towards high electrical conductivities is found in these areas. The use of values for only those profiles with no detectable gypsum failed to eliminate these anomalies. Examination of the 1 : 1 water-extract analyses for these soils in horizons close to the gypsum bed showed evidence for the accumulation of considerable quantities of sodium and magnesium sulphates in the overlying soil (Table 3).

It will be observed that three of these soils have a moderate salt content of the subsoil at depths below a metre or so, the total dissolved salts being a few thousand parts per million, say, 0·2 to 0·5 per cent., reckoned on the dry soil. These gypseous horizons in a 1 : 1 extract

yield roughly equal parts of Ca, Mg, and Na to solution, the concentration of each being about 20 m.e./litre. These extracts are probably more or less saturated with gypsum, and some gypsum no doubt remains undissolved. Some of the Mg and Na in solution may be derived by base exchange occurring on addition of water to a soil containing gypsum,

TABLE 3

Results of 1 : 1 Soil Extract Analyses for Four Soils overlying the Gypsum Bed, Kirkuk Plain

Pit	Depth (cm.)	Field no.	E.C. 10^4 mmhos/cm.	Soluble salts m.e./litre								T.D.S. p.p.m.
				Cations				Anions				
				Ca^{++}	Mg^{++}	Na^{+}	Total	Cl^{-}	SO_4^{--}	HCO_3^{-}	NO_3^{-}	Total
R2	0–15	9	1,100	2·0	2·4	6·5	10·9	5·0	3·4	1·6	1·2	11·2	650
	15–55	10	5,500	3·2	2·8	50·0	56·0	40·5	14·2	1·5	1·1	57·3	3,350
	55–90	11	>15,000	32·0	12·0	190·0	234·0	149·2	85·4	1·0	1·4	238·0	14,000
	90–150	12	>15,000	28·0	24·0	203·0	255·0	169·0	82·8	1·0	1·9	254·7	15,040
	150–183	13	>15,000	30·0	22·0	235·0	287·0	211·2	71·4	1·0	1·9	255·5	17,100
R12	0–15	69	350	2·0	0·8	0·6	3·4	0·7	1·2	1·3	0·1	3·3	325
	15–70	70	550	3·6	0·8	1·2	5·6	0·6	3·4	1·6	0·0	5·6	580
	70–150	71	2,500	28·0	7·2	2·9	38·1	1·2	35·0	1·3	0·2	37·7	2,875
	150–200	72	2,800	27·6	14·8	5·6	48·0	3·0	40·8	1·1	0·6	50·5	3,065
	250–300	73	3,500	25·2	21·2	9·2	55·6	3·0	52·2	1·1	0·8	57·1	4,275
	350–400	74	3,600	24·0	25·6	17·0	66·6	3·3	59·6	1·3	1·1	65·3	4,935
	450–500	75	4,300	23·6	23·6	20·0	67·2	3·9	60·0	1·0	1·1	66·0	5,060
R85	0–18	566	520	3·6	0·8	1·0	6·3	0·9	3·4	2·0	0·3	6·6	515
	18–48	567	650	2·4	2·4	2·0	6·8	1·8	2·4	2·0	0·5	6·7	530
	48–82	568	1,200	4·0	2·4	5·8	12·2	1·5	8·0	2·8	0·2	12·5	910
	92–128	569	2,400	10·0	10·4	10·8	31·2	2·1	27·6	2·1	0·2	32·0	2,600
	128–150	570	1,900	4·8	7·2	11·5	23·5	2·4	17·8	1·8	0·2	22·2	1,960
	155–167	571	1,900	6·0	6·0	10·8	22·8	4·8	16·2	1·8	0·2	23·0	1,600
	167–200	572	1,700	4·8	5·2	9·6	19·6	5·4	11·4	2·0	0·3	19·1	1,260
	290–320	573	2,800	11·2	10·4	14·9	36·5	3·0	32·2	2·0	0·2	37·4	2,615
	350–400	574	2,800	7·6	10·4	19·0	37·0	3·3	30·8	2·0	0·2	36·3	2,545
	450–500	575	8,000	8·0	12·4	19·7	40·1	3·3	26·0	1·8	0·1	41·2	3,010
R255	0–10	1,286	600	3·2	1·6	0·6	5·4	0·6	2·4	1·5	1·2	5·7	550
	20–78	1,287	600	3·6	1·2	1·0	5·8	1·2	2·0	1·6	1·3	6·1	530
	78–120	1,288	900	5·6	2·0	2·2	9·8	1·5	6·0	1·3	1·4	10·2	710
	120–200	1,289	2,800	20·8	10·0	6·9	43·7	2·1	37·8	1·5	1·6	43·0	3,375
	270–300	1,290	4,200	23·6	24·4	18·5	66·5	4·5	57·0	1·5	1·8	64·8	4,800
	370–400	1,291	4,700	20·4	27·2	27·8	75·4	6·0	62·0	1·3	1·1	70·4	5,405

but even at low moisture content some magnesium and sodium may well be present in ionic form. By contrast soil R2 evidently contains sodium chloride as a major constituent. In comparison with gypsum, sodium chloride must be regarded as a mobile constituent. The analyses seem to justify the present discussion, which refers mainly to the major features in the present distribution of the relatively mobile soluble salts.

4. *Nearness to marked gully systems*

When an open drain is excavated in saline land, a decrease in salinity may be found near the drain, due to the action of rain which leaches the soluble salts out of the surrounding soil (Hulsbos, 1958).

This effect is also to be seen in certain areas of the Kirkuk Plain. South of Dibbis, a salinity only slightly exceeding 2 mmhos/cm. is found where an undissected alluvial plain lies between the gully erosion spreading in from the Lesser Zab on the one hand and the Zighaitun Chai on the other. A similar small but noticeable effect is seen around

the northernmost area of shallow soils over gypseous alluvium west of the Jebel Batawa.

In the centre of the area no such effect is noticeable, but this may be due to the high salinity and the fact that gullies form the boundaries between the areas irrigated from various sources. The deep gullying in the area irrigated by the Tauq Chai may have contributed to the low salinities there.

Certainly the presence of the deep gully system in the area must have contributed to producing the present low water tables over much of the area.

5. *Depth to the water table*

Fig. 3 shows the depth of the water table below the ground surface over much of the area. The observations were made in late March when the water table was at its highest. Just what seasonal variation occurs in this area is uncertain, but experience near Baghdad suggests a range of variation up to 1·0 m. Also shown on it is the area of saline soils (electrical conductivity (extract)—more than 15 mmhos/cm.). There is a remarkably good agreement between the present high-water-table areas and the presently saline soils. The latter occur in a limited region bearing no obvious relationship to past irrigation history. It would therefore appear that these soils are the result of the present high water table. Before leaving this subject, it is worth noting the relationship between soil salinity in the top 50 cm. and water-table depth (Fig. 4). This diagram is the result of plotting corrected average salinities of the 0–50-cm. layer of soil against the depth to the water table. The correction consisted of modifying the actual value to that which would be expected if the water table was of a uniform salinity of 1,000 mmhos/cm. Although depths below 2 m. are usually considered fairly safe, this does not appear to hold good in the present case. This may be connected with the very recent imposition of a leaching process which may not yet have produced a true equilibrium between the depth of the water table and surface salinity. Saline soils overlying a deep water table are also a widespread phenomenon in the desert areas of N. Iraq, so that this could alternatively be due to a dry zone between the water table and surface horizons preventing leaching. Probably both causes are involved. Most of the saline soils of the non-irrigated areas of Iraq exhibit similar depth-salinity régimes, but it is doubtful whether all of them have only recently come under leaching conditions. One other common factor is the presence of a relatively dry zone at all seasons of the year between the surface horizons and the moist gleyed soil immediately above the water table. Once such a dry zone had developed, leaching of the surface horizons would be impossible until this dry zone again became moist. This would explain why some of the soils of the Hawija area are not very saline in spite of the high water tables occurring there (see Fig. 3).

6. *Salinity of the groundwater*

The only anomalies in salinity distribution that remain unexplained are the patches of relatively saline areas (E.C. greater than 6 mmhos/cm.),

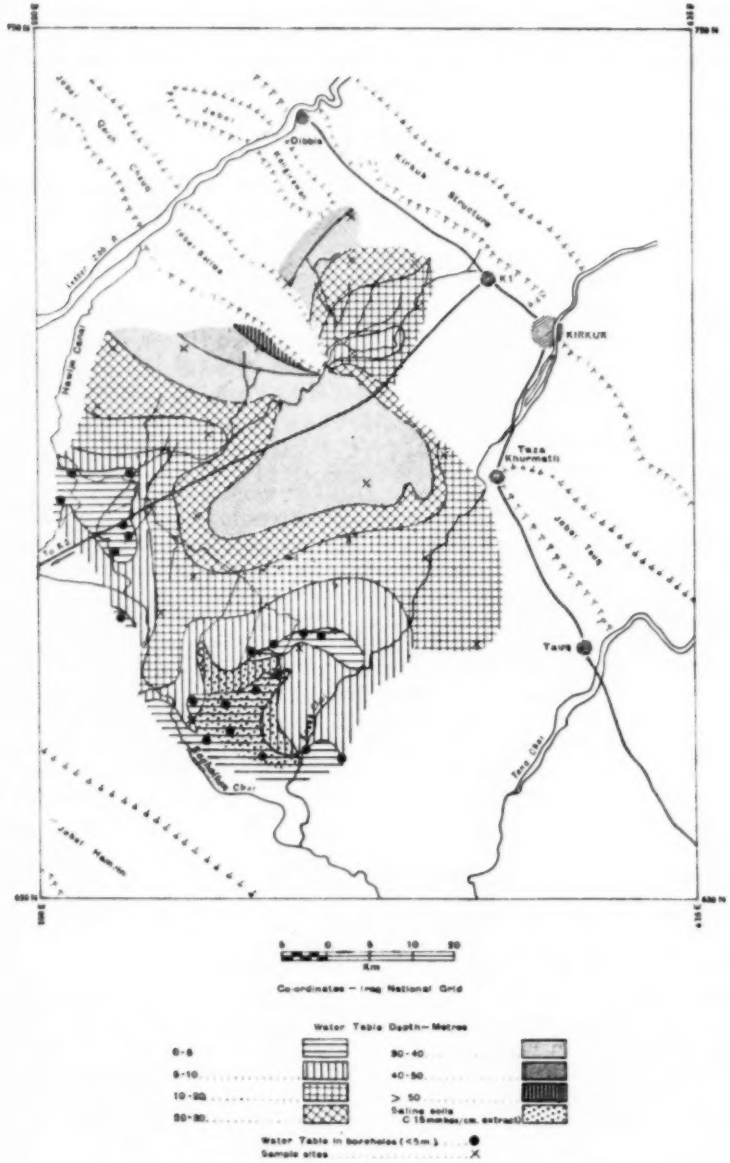

FIG. 3. Depths to the water table in the Kirkuk Plain.

south of the Pipeline Road, in the centre of the area. Comparison of these areas with the areas of high salinity in the groundwater (Fig. 5) shows that they overlap one another. Furthermore, the loop of the

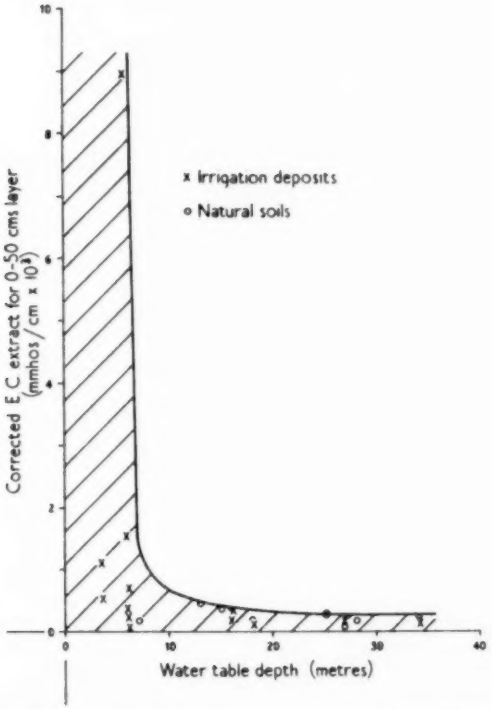

FIG. 4. Relationship between surface salinity and height of the water table in the non-gypseous alluvial soils of the Kirkuk Plain. The salinity value for the 0–50-cm. horizon has been corrected to a constant E.C. of the water-table of 1 mmho/cm. ($\times 10^3$).

8-mmhos/cm. salinity contour which crosses the area irrigated in the past by the Khasa Chai coincides with the area of highest salinity of the underground water. Since desalinization is of widespread occurrence, the groundwater must be becoming more saline during its journey across the area. Thus this correlation of the salinities of the water table and soils may be due to the leaching process, and the groundwater may be more saline today than it has been in the past.

Classification of these Soils

There seems to be evidence to suggest a division of saline soils into 'Active Saline Soils' and 'Remanent Saline Soils'. In the former, the water

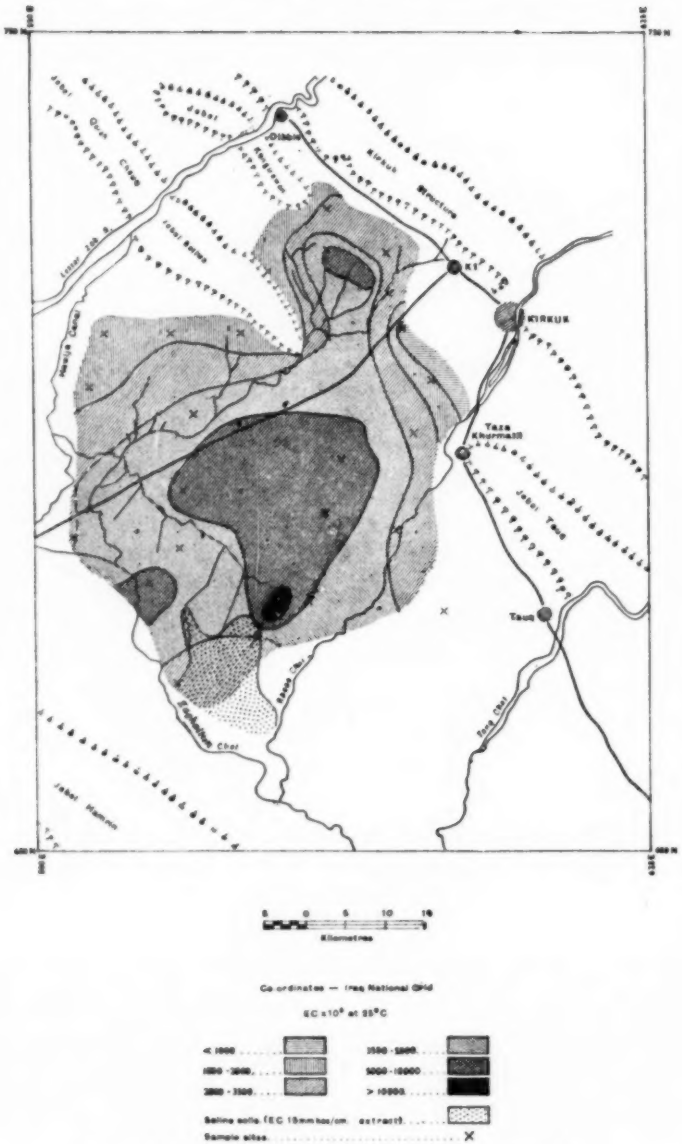
KIRKUK
Tuza Khurmatli
Tuza
Jebel Hamrin
Kirkuk Structure
Jebel Gurn Ciceen
Jebel Ramas
Jebel Tuza
Tuza Chai
Tang Chai
Kirkuk
Kirkuk
Kirkuk

table stands at a very shallow depth (less than 2 m.) and gley phenomena occur in the solum. In the remanent saline soils the profile is usually fairly dry except for the surface horizons after rain. Groundwater gleying occurs only at considerable depths close to the deep water table.

The ready leaching under irrigation of the remanent saline soils means that for irrigation purposes, they should be given a different land classification to the active saline soils. Even dense, badly structured remanent saline soils with high exchangeable sodium are readily leached in Iraq and so it would seem better for irrigation purposes to put these soils in Land Class 3 (Water Table surface at 2–5 m.) or Land Class 2 (Water Table surface below 5 m.).

Origin of the Salt

On palaeogeographic grounds the salt cannot be cyclic (i.e. blown inland as spray from the sea) nor can it have been deposited with the alluvium.

From the foregoing discussion, it is apparent that the accumulation of salts in the soil is primarily the effect of the high water tables. This is modified by other factors such as the salinity of the water table, &c. Figs. 3 and 5 suggest that the origin of the water in the water table is by seepage from the rivers and jebels, since the salinity of the water table decreases towards the jebels and the perennial rivers. Highest salinities occur in the centre of the area, although the water there cannot be static (Fig. 6). In fact, the surface of the water table has at least a moderate slope everywhere.

The only effect of a deep water table is to limit the degree of desalinization which may occur. On the other hand, the desalinization process adds a considerable quantity of salts to the water table. Salts are also added to the water by dissolving the gypsum bed through which it passes. The relative importance of these processes may be gauged by plotting the percentages of sulphate and chloride ions present against total anion concentration. The results suggest that solution of gypsum is the dominant cause of increase in groundwater salinity at first, but above a total anion concentration of about 54 m.e./litre, addition of salts is mainly due to desalinization.

The water in the jebels comes from rain water and plutonic water. The composition of the latter shows considerable variability but is lacking in sodium and chloride ions (two examples will be found in Table 1). A fantastic quantity of water would be necessary to provide the required salinity of the ground water, while considerable quantities of calcium and magnesium sulphates would have to be precipitated from solution. There is little evidence for this. Rainwater would collect certain ions during its passage through the atmosphere, but sodium and chloride ions would not be added in this way. It must therefore be concluded that the fresh groundwater acquires both sodium and chloride ions on its way through the rocks forming the jebels to the alluvium. Thus it must dissolve common salt from the Fars beds through which it passes.

The river waters are the result of runoff from rain, melt water from snow, and underground drainage water from the Miocene and earlier

rocks of the catchment area. The runoff is usually of short duration, causing a flood. Meltwater is important in the spring and summer, but the mainstay of the perennial rivers is the drainage water which has

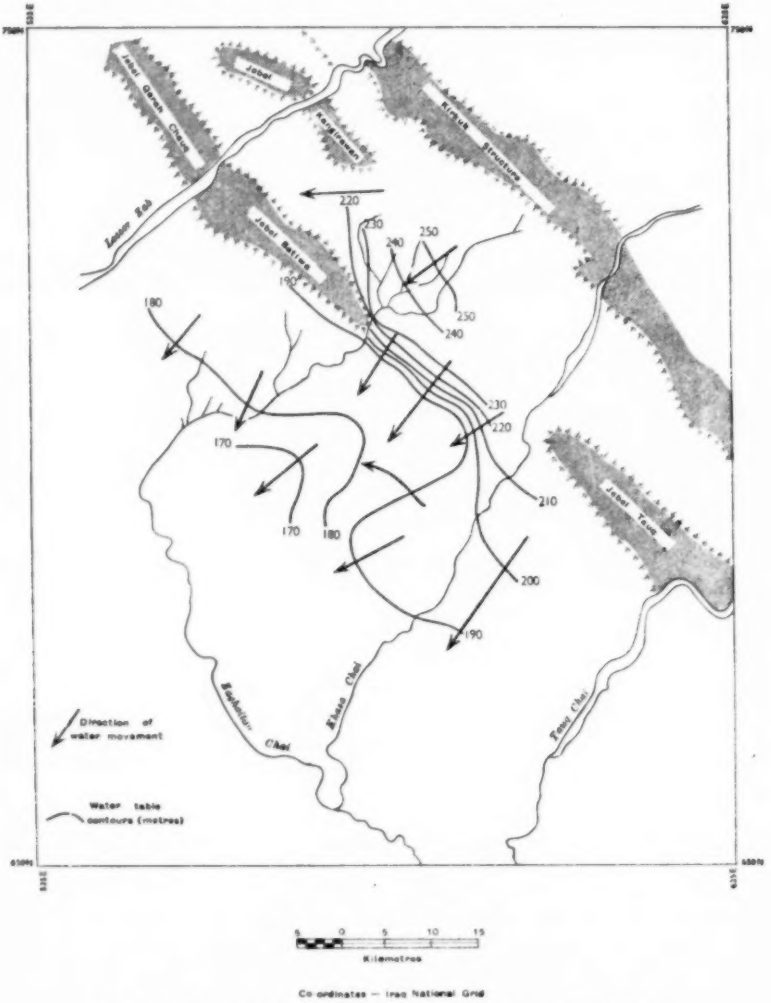

FIG. 6. Contours of the water table in part of the Kirkuk Plain.

entered the rocks forming the hills and mountains, passed through the rocks and has then reappeared as springs. Once again, the only source for the salts is the rocks through which the water passes. This bears out the ideas of Smith (1957, p. 109) as to the ultimate origin of the salinity.

Conclusions

1. The salts chiefly originate from the Fars beds in the jebels, where they were originally formed by the evaporation of remnants of the Tethys. Additions of plutonic water are small and of little importance.

2. Ground and surface waters dissolve these salts and migrate southwards either in rivers or else underground into the margins of the Kirkuk Plain. The best source of water appears to be from the neighbourhood of Kirkuk. Loss of water by the perennial streams due to percolation underground may have a considerable effect on the groundwater.

3. This groundwater is the ultimate cause of salinization. Both depth to water table and salinity are important during salinization. The salinity of the underground water depends on how far it has travelled through the gypsum bed and the quantities of salt added due to the leaching process.

4. The area consists of both natural soils and soils formed on irrigation deposits. In the latter, considerable accumulation of soluble salts has occurred compared with the natural soils.

5. The quality of the irrigation water in both present-day and past irrigation areas is excellent and is not thought to be an important factor controlling the degree of soil salinity. Minor factors include the presence of deep gullies which act as drains, and the existence of a gypseous horizon in some places within 60 cm. of the surface. Lack of drains and use of too little water to remove salts are perhaps mainly responsible for present salinity.

6. Salinization of the irrigation deposits with slight salinization of the natural soils occurred until the end of the first phase of irrigation.

7. This was followed by initiation or rejuvenation of the wadi systems. This was probably connected with uplift of the northern end of the area and the movement of the Tigris into its present course (*c.* A.D. 1242). Since then, desalinization has occurred as the level of the water table dropped in all except an area of slight subsidence in the south-west. There, salinization continues. This desalinization process may not yet have proceeded far enough for a true equilibrium to be established between the surface soil salinity and the depth to the water table. This could be due to a dry zone of soil between the surface layers and the water table.

8. Local accumulation of salts is now occurring in two areas near the jebels, watered predominantly by underground waters without a drainage system.

9. The saline soils may now be divided into two distinct groups, viz. the active saline soils found in certain of the presently irrigated areas, and the remanent saline soils with deep water tables.

Acknowledgements

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SOILS OF THE QUEEN ELIZABETH ISLANDS (CANADIAN ARCTIC)

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(*Saskatoon*)

Summary

A geological reconnaissance of the northernmost group of islands of the Canadian Arctic (Queen Elizabeth Islands) afforded an opportunity to study the nature of the soils. Profile development is rare, and the nature of the soil surface mainly depends on the slope of the ground and the type of bedrock. Chemical weathering and plant action are almost negligible in the arctic environment. Three profiles were examined in detail, two in well-drained positions and one probably waterlogged for most of the thaw period.

It is concluded that soils of this area should properly be regarded as polar equivalents of lithosols and regosols and that they should not be classed with the Tundra Great Soil Group. The name Rawmark Great Soil Group is suggested to encompass such soils of polar environment both in the northern and southern hemispheres.

Introduction

DURING the 1955 field season the Geological Survey of Canada conducted a geological reconnaissance, known as Operation Franklin, of the Queen Elizabeth Islands, the northernmost group of islands belonging to the Canadian Arctic Archipelago (Fig. 1). While participating in the survey the author was able to make brief observations of the soils in some of the regions visited.

No doubt casual soil investigations have been made before by other workers in the Queen Elizabeth Islands, but locations of observations and descriptions of the soils have not been published except for the work of Feustel *et al.* (1939). Material on which their work was based included samples from one location on the southern part of Ellesmere Island and one place on the large island directly south (Devon Island). Samples were taken during the 1955 survey for study of clay minerals, but the present paper is meant to describe the environment and nature of three soil profiles from which clay minerals were obtained and to discuss their significance.

Physiography

A brief summary of the surface features, climate, and vegetative cover of the Queen Elizabeth Islands is given below.

Ellesmere and Axel Heiberg Islands are mountainous, with elevations commonly exceeding 6,000 ft. The other islands, in general, consist of open, gently undulating plains interrupted by steep hills and escarpments. Maximum elevations are generally less than 1,500 ft. and on the plains between 100 and 500 ft.

The higher areas of Ellesmere and Axel Heiberg Islands are occupied by permanent snow fields which nourish hundreds of valley glaciers. On the western part of Axel Heiberg Island, north of Strand Fiord, several glaciers issuing from the mountains merge to form a piedmont

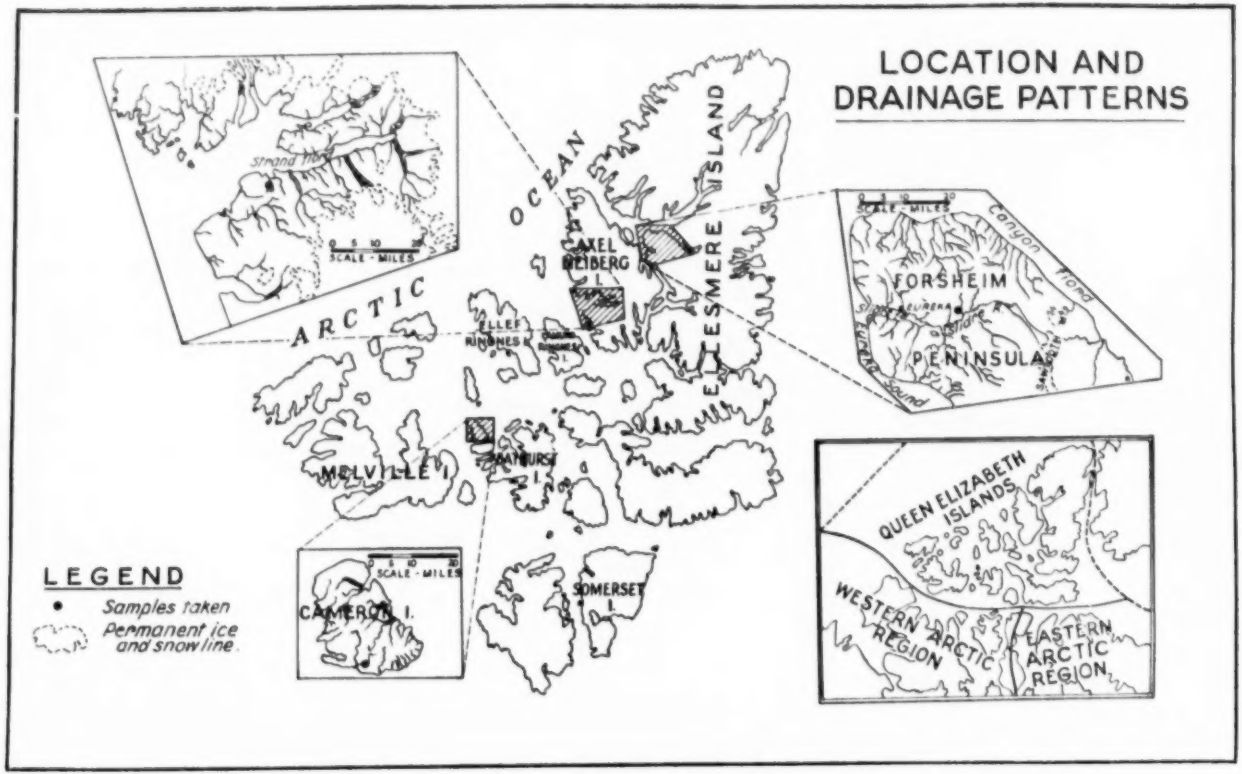

LOCATION AND
DRAINAGE PATTERNS
ARCTIC OCEAN
ELLESMERE ISLAND
AXEL HEIBERG I.
ELLEF RINGNES I.
MELVILLE I.
MATHURSTI.
CAMERON I.
SOMERSET I.
SCALE - MILES
FORSHEIM PENINSULA
Canyon Fiord
Strand Fiord
Eureka Sound
QUEEN ELIZABETH ISLANDS
WESTERN ARCTIC REGION
EASTERN ARCTIC REGION
LEGEND
Samples taken
Permanent ice and snow line

FIG. 1

glacier. Other islands lose most of their snowfields in mid-July. Islands of the north-western part of the Queen Elizabeths, on the edge of the Arctic Ocean, have a much shorter summer than islands to the south-east.

Meteorological observations have been made at widely separated stations in the Canadian Arctic Islands for only a few years. A summary of the climate as it has been found from these observations has been published by the Canadian Department of Transport (Rae, 1951). In general, winter conditions prevail from October to May. June and September are transitional periods. July and August can be considered as summer although snowstorms are common, as are frosts at night.

Darkness prevails all winter and continuous light occurs for less than half of the year. During the light period, particularly after large patches of open water appear in the fiords and sounds, approximately half of the summer days are misty. Mists commonly prevail for several days (sometimes up to a week) in one area.

The rigorous climate restricts chemical weathering and plant growth, the effects of which on the character of the ground surface is negligible. Because of these conditions and the fact that there are no extensive areas of ground moraine, the nature of the ground surface, or soil, is controlled by its slope and by the bedrock of the immediate vicinity.

The following consideration illustrates how slope is a dominant factor controlling the nature of the ground surface. The bedrock of Ellef Ringnes and Amund Ringnes Islands is mainly shale and sandstone. These islands are low with few steep gradients so that the upper foot of unfrozen ground is waterlogged and sticky, particularly in areas underlain by shale. In contrast, on steep slopes of Axel Heiberg Island underlain by the same shaly rock formations the unfrozen ground is well drained, fragmental, and not sticky. The permafrost layer at about 18 in. depth allows only surface and near-surface drainage.

To illustrate that the variations in bedrock have a great effect on the flat ground surfaces, the northern part of Somerset Island and Ellef Ringnes Island can be contrasted (Plate I). The northern part of Somerset Island is underlain mainly by hard calcareous shale and limestone which do not weather to clay-size particles in the Arctic environment. Chemical action of the atmosphere on the bedrock and the action of plants are apparently negligible. Drainage is efficient and waterlogging is confined to the bottoms of topographical depressions. On the other hand the flat parts of Ellef Ringnes Island underlain by softer shale is sticky and waterlogged because the clay particles retain moisture and impede drainage.

Polygonal patterns occur in almost all fairly flat areas of the Arctic. Stone strips are the rule on slopes. The reader is referred to Washburn (1956) for the most up-to-date information on the topic of patterned ground.

Except in rare cases the vegetative cover of the ground in all the area is not closed. In low, poorly drained patches, rarely exceeding 100 ft. across, a continuous thin veneer of moss can occur. Elsewhere mosses, grasses. Arctic willow, and other plants do not form a ground cover,

but each individual plant or colony is separated from another by several inches to several feet of bare earth or rock.

Description of Soils

Soil from Slidre River area

Situation (Fig. 1). The region on Forsheim Peninsula, in the western part of Ellesmere Island lying between Slidre Fiord and the Sawtooth Mountains, is for the most part a gently undulating plain with rounded hills up to 500 ft. high. It is drained by Slidre River and its tributaries which assume a crude trellis drainage pattern. The pattern is controlled by folded Lower Tertiary continental beds referred to as the Eureka Sound formation. The rocks are mainly grey sandstone, siltstone, and lignite. Except for a few bands, the sequence is non-calcareous.

In July the main trunk stream, Slidre River, flows fairly swiftly and is almost 100 ft. wide and from 3 to 6 ft. deep. It is a mature stream with some meanders incised into the folded Eureka Sound formation and the flat-lying bedded Pleistocene sand overlying the bedrock. At least one terrace exists in the valley, but slight uplift of the area has caused the initiation of the present downcutting.

Slidre River flows continuously during the melting period of the year because it is fed by waters from the snowfields of the Sawtooth Mountains to the east. Unlike the Slidre River, the stream branches of this main trunk flow for only a short time during the year because they are nourished only by small snowdrifts which soon melt, and by ice wedges within the Pleistocene alluvium.

The surface of the uplands between the stream channels in many places is covered by a thin discontinuous sheet of white salt. In some places it tastes like sodium chloride, elsewhere like magnesium sulphate. These patches are particularly common where tiny rivulets drain from the uplands to a stream channel.

It is tentatively judged that in Pleistocene or Recent time an arm of the sea stretched from Slidre Fiord and covered this flat undulating area and perhaps joined Canyon Fiord making Forsheim Peninsula an island separate from Ellesmere. Basis for this judgement is found in the nature of the salt in the alluvium and the even bedding of the alluvium.

Much of the ground surface is patterned with polygons averaging 50 ft. in diameter. The polygons are separated from each other by depressions 2 ft. deep and 1–3 ft. wide. The centres of the polygons are bowed up resembling inverted saucers. In July perma-frost occurs at a depth of 16–19 in. near the centre of the polygons and about 4 in. at the margin. These large polygons commonly are composed of hundreds of small ones which average 12 in. across and 10 in. high. This imparts a very rough surface to the ground.

The vegetative cover of the area is discontinuous, but the countryside does possess an overall green appearance. Patches several hundreds of feet across occur that have little or no vegetation. In sheltered areas Arctic willow, Arctic aven, and short grasses occur individually or in tiny colonies and are separated from each other by bare ground. Arctic

willow grows along the ground, commonly for 4 or more feet. The diameter of willow rarely exceeds that of a broom handle.

Profile (Plate I*c*). A soil profile was examined on the west bank of a tributary of Slidre River approximately 1½ miles north of the junction. The hole was dug near the centre of a polygon on a slope 8° to the south-west.

No horizon development could be observed. The permafrost occurs at a depth of 16 in. and the soil above is well drained. The upper 8 in. is slightly more effervescent with dilute hydrochloric acid than the lower 8 in. of unfrozen ground. The parent material is medium sand composed of quartz, feldspar, mica, and occasional tiny coal fragments. The soil possesses no humus or litter horizon. One spherical patch of shotty structure 2 in. in diameter occurred at 7 in. depth. It is composed of $\frac{1}{16}$–$\frac{1}{8}$-in. clayey, dark grey, waxy pellets. An origin for this patch in this profile is not suggested.

The pH of the top 8 in. is 7·9 and that of the 8–16 in. depth is 8·0. These two arbitrary intervals contain 0·22 per cent. and 0·17 per cent. nitrogen respectively.

Soil from Strand Fiord area

Situation (Fig. 1). Strand Fiord projects into the south-western part of Axel Heiberg Island. The area investigated is along a northward-flowing stream approximately ½ mile south of the mouth of the fiord.

The bedrock of the vicinity is grey, calcareous to non-calcareous shale, and light brown and grey sandstone intruded by diabase sills up to 200 ft. thick. The shale and sandstone beds are a marine and continental sequence belonging to the Triassic, Jurassic, and Cretaceous Systems. The rocks of the neighbourhood of Strand Fiord have several structural domes containing gypsum cores (diapirs) which incorporate blocks of limestone containing Palaeozoic fossils.

Hills in the immediate vicinity of the location where the soil was sampled are steep and attain approximate elevations of 2,000 ft. A rubbly surface of bare rock prevails. The mountains surrounding Strand Fiord are separated from each other by active glaciers which at lower elevations melt and supply the numerous streams for the whole of the thawing period of the year.

The lower valley of the stream indicated on the map (Fig. 1) is bounded on the west by steep bare slopes of a gypsum dome. The eastern valley wall consists of 50 ft. of horizontally bedded alluvium comprising sand and silt which the present drainage is dissecting. The fairly even valley floor is 200–500 yds. wide. The stream is not as swiftly flowing as farther inland, and, because of the evenness of the valley floor, the unsorted cobbly alluvium is waterlogged for all or most of the thaw season.

Profile. Samples were taken of soil in a patch 75 ft. across having a peaty layer an inch or two below the surface of a pool of stagnant water. The surface of the water is covered with a film of iron oxide.

No soil profile development was observed. The permafrost occurs at a depth of 16 in. and the soil above is water-saturated, unsorted alluvium.

The pH of the top 8 in. is 7·1 and of the 8–16 in. depth is 7·6. The nitrogen content of these same two intervals is 0·20 and 0·07 per cent. respectively.

Soil from Cameron Island

Situation (Fig. 1). Cameron Island is a relatively small island of the Queen Elizabeth group situated approximately halfway between the northern parts of Bathurst and Melville Islands. The area investigated is in the southern part of the island along a stream flowing southwestward.

The southern part of Cameron Island is underlain by folded sandstone and shale of the Devonian and Permian Systems. To the north lie sandstone and shale, for the most part not highly folded and in general not indurated, classed as Mesozoic. The rocks of the immediate vicinity where soil was sampled are grey and brown calcareous sandstone belonging to the Devonian System.

The topography of the southern part of Cameron Island is mature, being composed of gently rounded hills, not exceeding a few hundred feet high, separated from each other by meandering streams. The hills are not high enough for permanent snowfields to develop. Consequently, owing to the melting from winter snow, the streams are full in July and part of August, but relatively empty in late summer when the only water supply is seepage from springs fed by melting ice wedges and permafrost.

Vegetation consists of a continuous cover of mosses, short grasses, and minor Arctic willow which grows along the ground. The hilltops and valleys alike have a vegetative cover. Some sand slopes, which are of limited extent, do not support a plant cover of any kind. When dried out these sandy patches blow out readily.

The streams are fairly fast-flowing and alluvial terraces are common 5 or 6 miles from their mouths. The terraces are bedded gravel and sand which produce even surfaces between the stream channel and the base of the hills. In most places the terraces have a gentle tilt toward the stream channel. The soil profile examined is on a small alluvial terrace.

It is judged that the soil environment described is well drained during July and August, but the time of examination in early September was after a snowfall and the melting snow caused a saturated profile.

Profile (Plate I *d*). The profile was examined on a gently sloping terrace about 5 ft. above the stream bed and 100 ft. north of it at a point approximately midway between two major bends in the stream. Slight horizon development has taken place. The profile includes 9 inches of non-calcareous medium to coarse silty brown sand overlying a darker brown pebbly gravel. The pebbles are mainly rounded olive-green sandstone which are separated from each other by sandy material similar to the non-pebbly alluvium above. The upper surface of the permafrost occurs at a depth of 18 in.

The top 2 in. of the soil consist of a green-brown sand containing peaty fragments dispersed throughout, and predominating at the sur-

face. This thin layer, comprising a very thin and discontinuous A_0 and a discontinuous leached A_2 is light grey in colour. The horizon below is brown, structureless, non-calcareous silty sand 7 in. thick overlain by a gravelly layer of unknown thickness. This profile may represent a primitive podzol.

The pH values for the 0–2, 2–9, and 9–18 in. segments of the profile are 6·0, 5·7, and 5·7 respectively. The nitrogen contents are 0·26, 0·05, and 0·06 per cent.

Discussion

The preceding remarks and observations lead the author to believe that previous classification of Arctic soils by most other authors is in need of revision. It is clear that there are no soils belonging to the Tundra Great Soil Group in the Queen Elizabeth Islands. The Tundra soil is frozen for most of the year and rests on permafrost. Except in tiny isolated places, nothing of the sort is observed in the Queen Elizabeth Islands. Nevertheless, in most textbooks and articles written by North Americans dealing with the soils of the world in general the soils of the Arctic are referred to as Tundra soils. For instance, Lyon and Buckman (1947) state that Tundra soils lie just north of the Podzolic group, but no mention is made of what lies north of the Tundra. More recently Winters and Simonson (1951) published a map which classes the soils of the Queen Elizabeths as Tundra soils. They seem to base their statement that the region is Tundra on pioneer work done by Fuestel *et al.* (1939). Winters and Simonson fail to qualify Fuestel's work by acknowledging that most of the samples were taken from small depressions where peat could accumulate, mainly in the Subarctic region. Furthermore, Fuestel *et al.* state that the soils may perhaps be regarded logically as 'lithosol associates of what is recognized as true tundra'.

The frontispiece of *Plant Ecology* by Weaver and Clements (1938) furnished an example of how the wrong view has expanded into other sciences. Weaver and Clements (p. 199) state that Tundra soils lie north of the Podzols. They extrapolate and assume that all the soils of this vast area are within the same climatic belt and support the Tundra climax. The Canadian Arctic Islands probably embrace more than one climatic type, and latitude is by no means the main control. In some seasons ships can sail to the northern tip of Ellesmere Island and Eureka, but at no time are the frozen seas around Ellef Ringnes Island navigable. Vegetation on the western side of Axel Heiberg Island is retarded in comparison with that of the area around Eureka.

Tedrow *et al.* (1958) contend that Tundra soil should not properly be considered a Great Soil Group, and suggest that the term should be relegated to apply primarily to northern analogues of the hydromorphic soils of the forested regions. This author does not subscribe to the views of Tedrow *et al.*, and accepts the view that a tundra girdle does exist beyond the Podzols in most places in the world.

Kubiena (1953, pp. 108, 146–9) does distinguish between the 'tundra girdle' and the raw soil in the 'region of the melting soils of the Arctic'.

He classes the terrestrial soils of the islands of the Polar seas as Raw Soil of the Cold Desert (Rawmark). This 'type' includes three 'varieties' in the Arctic areas, Arctic Frost Earth (Common Arctic Rawmark), Arctic Hamada Raw Soil (Arctic Hamada Rawmark), and Structure Soil (Structure Rawmark). Semi-terrestrial soils of the Arctic that have a non-gravelly alluvium parent material and develop patterned ground are termed Arctic Rutmark by Kubiena.

A summary of the characteristics of the four Arctic soils considered by Kubiena follows:

Arctic Frost Earth. The soil supports a plant cover which is never closed. Usually a distinct A horizon forms which is underlain by a C_1 horizon which separates it from permafrost. Although the profile is waterlogged for most of the summer, no gleying occurs because of the low chemical weathering. At the best the texture is gravelly, sandy grit of light or dark brown colour.

Arctic Hamada Raw Soil. The hamada can be one pebble layer deep or several feet. Finer fractions are removed by wind. This layer rests on a C_1 horizon which is bounded below by permafrost. Small earth islands support higher plants, or they may root in the C_1 horizon.

Structure Soil. This soil is patterned ground derived from gravelly Frost Earth or Hamada Raw Soil. The margins of polygons or stripes are lined with stones or cobbles.

Arctic Rutmark. Stone-free alluvium which forms patterned ground on what Kubiena classes as semi-terrestrial soil is called Arctic Rutmark (Kubiena, 1953). It is distinguished from Structure Soil by lack of stone boundaries between the polygons.

The soil described from Cameron Island can be classed as Arctic Frost Earth. It has an A horizon and the ground is not patterned. The soils described in this paper from Slidre River area and Strand Fiord cannot be accommodated within Kubiena's divisions. The Slidre River terrestrial soil, although having stone-free patterned ground characteristic of Arctic Rutmark, is not in that division. The Strand Fiord soil is waterlogged or frozen for the whole year. Assuming that it did drain from time to time (semi-terrestrial) it still cannot be properly classed as Arctic Rutmark because the parent material is not stone-free. If the area was patterned the margins of the polygons most surely would be lined with stones.

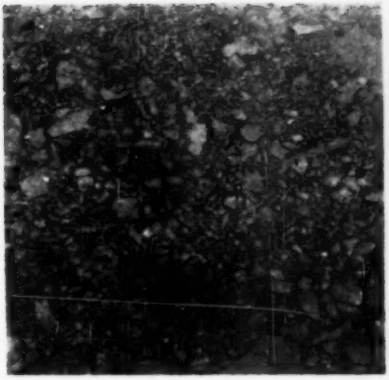
Conclusions

1. It is suggested that the term 'Tundra' should not encompass all the soils north (or south in the southern hemisphere) of the Podzol zone, but should be restricted to refer to peaty or semi-peaty soils of that area.

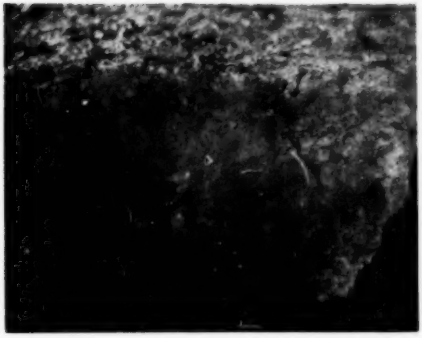
2. Further, it should be recognized that the non-peaty soils in Polar areas are in reality mainly similar to lithosols and regosols of the temperate zone.

3. Soils of higher latitudes than Tundra are zonal and should represent a great soil group. The name Rawmark Great Soil Group is suggested.

(*a*) Poorly drained area of Amund Ringnes Island underlain by shale



(*b*) Hamada of the arctic desert underlain by shaly limestone on Somerset Island



(*c*) An exposure showing lack of profile development near Slidre River on Ellesmere Island

(*d*) A primitive podzol on Cameron Island. Note the slight leaching at the surface next below the thin peaty veneer

N. J. McMILLAN—Plate I

Acknowledgements

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IRON AND THE E_h OF WATERLOGGED SOILS WITH PARTICULAR REFERENCE TO PADDY

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Summary

Assuming a simple ferro-ferric redox system in a waterlogged soil containing active organic matter, the equation $E_h = (1{\cdot}28 \pm 0{\cdot}03) - 3 \times 2{\cdot}303 \frac{RT}{F}$pH is derived and some evidence is brought to support it.

The term $3 \times 2{\cdot}303 \frac{RT}{F}$ pH is three times greater than that commonly used when adjusting soil E_h measurements for pH change.

The author recommends that both E_h and pH values should be invariably quoted as measured, and a third term included for the adjusted E_h if necessary.

The equation is also used to suggest the importance of pH changes when considering the movement and precipitation of iron in aerated soils.

WHEN reporting the E_h of waterlogged soils, particularly paddy soils, it has become the custom to adjust for pH variations by the term

$$1 \times 2{\cdot}303 \frac{RT}{F} \text{ pH}.$$

Evidence is brought here to show that the term $3 \times 2{\cdot}303 \frac{RT}{F}$ pH may be more exact.

The evidence, if correct, shows the overriding importance of the ferrous and ferric iron present when considering the oxidation-reduction chemistry of a waterlogged soil. Precise knowledge of this chemistry has been shown to be important when considering the availability of phosphate to paddy (Gasser, 1956), the toxic effect of sulphide (Mitsui, 1955; Shiori and Tanada, 1952), and the economic use of ammonium fertilizer (Mitsui, 1955; Mikkelsen and Finfrock, 1957).

Soil used

Pebbly silty clay loam, sieved to pass a 2-mm. sieve, from Cattlegate Farm, Northaw. Iron content 1·50 g. Fe/100 g. soil (by HCl digestion).

Organic matter used

1. Mixture of grasses obtained from Rothamsted Common.
2. Grass roots from Rothamsted Common, washed free from soil.

These were ground to a fine powder in a hammer mill after drying at 80° C. overnight.

Experimental Method

The changes in E_h and pH of the solutions above waterlogged samples of soil (30 g. soil + 250 ml. H_2O), having various additions of organic

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matter, were followed over periods of time, usually from 0 to 21 days after the initial submergence. The samples were kept in 450-ml. bottles with rubber stoppers equipped with tubes such that they could be completely swept out with nitrogen after each measurement. Therefore, except for the time to take each measurement, the samples were maintained under completely anaerobic conditions. The model 23A pH meter, of Electronic Instruments Ltd., Richmond, scaled to 0·1 pH unit and 0·01 volt, with bright Pt and glass electrodes against the saturated calomel electrode was used. A reading was normally taken three times (except for very low potentials) the sample being agitated and allowed to settle before each observation. Duplicate samples were set up for most experiments. The samples were stored in the laboratory at a reasonably constant room temperature of 22° C.

Results

Fig. 1 gives typical E_h against time curves for waterlogged samples: (*a*) 5 g. roots+250 ml. water only; (*b*) 30 g. soil+250 ml. water only; (*c*) 30 g. soil+5 g. roots+250 ml. water.

Duplicate pairs gave very nearly identical curves when both pots were done together. However, a duplicate pair, one being done in January 1957 and the other in March 1957 showed rather wide variation in period B, periods A and C were in good agreement.

The curve for soil and organic matter (1*c*) is characterized by an initial period, A, of intense reducing conditions and comparatively low poise, a second period, B, of very low poise and rapidly rising E_h, and a third period, C, where the values are easily determined and the poise is considered to be quite high. Changes in the poise were noted by the ease of making a reading. Crude redox titrations also gave evidence that C was a period of comparatively high poise (several ml. of dilute hydrogen peroxide required to give an inflexion) and A and B periods of low poise (one or two drops of hydrogen peroxide).

Fig. 2 gives two typical pH/time curves for samples undergoing initial submergence: (*a*) 30 g. soil+5 g. roots+250 ml. water; (*b*) 30 g. soil+5 g. grass+250 ml. water.

Further Treatment

Certain samples were further examined after their initial period of submergence.

The samples underwent an initial period of submergence for 21 days the E_h/time curves being determined, they were then subjected to a period of vigorous aeration, the samples being stirred and aerated by a continuous stream of air bubbles and, after 13 days, anaerobic conditions were restored, by stoppering and sweeping out with nitrogen, and the E_h/time curves again observed.

In all cases, after the onset of anaerobic conditions, the E_h/time curves moved gradually into period C, the curves being very similar to the 'soil only' plot above. There was no initial period, A, of intense reduction. The poise was high.

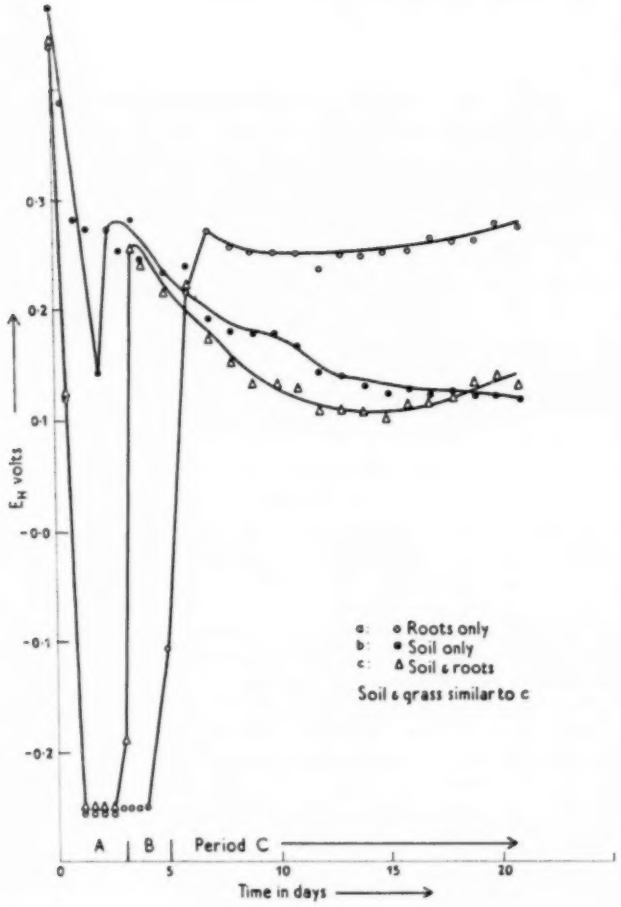
0·3
0·2
0·1
-0·0
-0·1
-0·2
E_H volts
a: ○ Roots only
b: ● Soil only
c: △ Soil & roots
Soil & grass similar to c
A
B
Period C
0
5
10
15
20
Time in days

FIG. 1

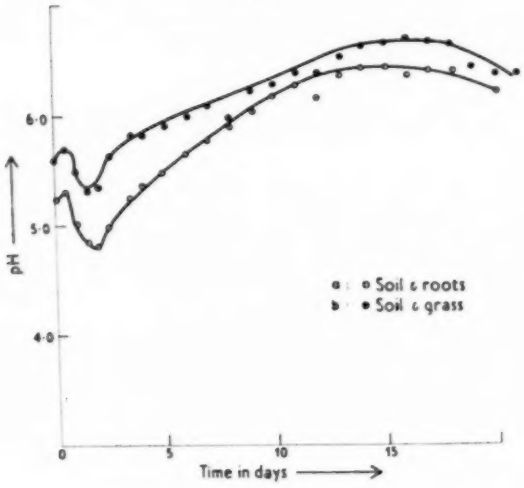
6·0
5·0
4·0
pH
a: ○ Soil & roots
b: ● Soil & grass
0
5
10
15
Time in days

FIG. 2

Discussion

From Fig. 1 we have:

(i) *For soil and organic matter together*

Period A. An initial period of intense reduction, E_h about −0·25 volt.
Period B. A release of systems of higher E_0 into the soil solution.
Period C. Establishment of a relatively well poised system at about 0·1 volt.

(ii) *For organic matter alone*

Period A. An initial period of intense reduction.
Periods B and C. A slower rise of E_h, after a longer period, A, to E_h values of about 0·26 volt. The system is never well poised.

(iii) *For soil only*

Periods A and B. A gradual lowering of E_h to about 0·1 volt.
Period C. Establishment of a rather ill poised system at about 0·1 volt.

(iv) *For soil and organic matter together submerged after initial oxidation treatments*

As for soil only, but in period C, the poise is much higher.

This suggests that, for soil and organic matter together, the period of intense reduction, A, is attributable to the fresh organic matter; the period B attributable to a release of systems, of comparatively high E_0, contained in the soil (as opposed to the organic matter), into the soil solution, and the period C to the establishment of a well poised redox system at about 0·1 volt derived from the soil, or, possibly, from the soil and organic matter together.

From other experiments it was found that in period B there was a rapid release of available iron, manganese being released during period A. This suggests that in period B the release of oxidizing materials involves the solution and reduction of solid iron oxides or hydroxides present in the soil. The gradual rise of the E_h for the organic matter on its own, Fig. 2*a*, is not explained, but it is suggested, since the poise of the system over the entire length of the curve is very poor indeed, that the small amount of air entering at each determination may be responsible.

Assuming that the dissolved iron does raise the E_h in period B and, furthermore, that it takes charge of the E_h in period C, then at low pH

$$E_h = 0{\cdot}771 + 0{\cdot}0585(\log a_{Fe^{+++}} - \log a_{Fe^{++}}), \text{ at } 22^\circ \text{ C. (Glasstone, p. 950).} \quad (1)$$

At higher pH, Fe^{+++} will be precipitated as the hydroxide; hence

$$0{\cdot}0585 \log a_{Fe^{+++}} = K - 3 \times 2{\cdot}303 \frac{RT}{F} \text{pH}, \quad (2)$$

where $$K = 0{\cdot}0585(\log f_{Fe^{+++}} - pK_{s Fe(OH)_3} + 3pK_w).$$

Taking $pK_s = 35{\cdot}58$, in solutions of ionic strength of about 0·2 (Evans and Pryor, 1949) gives

$$K = \text{about } 0{\cdot}289.$$

Combining the above equations gives

$$E_h = 1{\cdot}060 - 0{\cdot}0585 \log a_{Fe^{++}} - 3 \times 2{\cdot}303 \frac{RT}{F} \text{pH}. \qquad (3)$$

Schnitzer and Delong give iron in leaf extract solutions as 0·023 to 0·59 mg. ferrous iron per 140 ml. (3×10^{-6} to 8×10^{-5} mol./litre), which may be taken as marking the lower order of concentration of ferrous iron in the soil solution, since these extracts neither contained much fresh organic matter, necessary for the dynamic reducing activity of the bacteria, nor were they in contact with the ferric hydroxide for a great length of time.

Puustjärvi gives $c_{Fe^{++}} = 1{\cdot}9$ to $7{\cdot}3 \times 10^{-4}$ mol./litre (p. 39) in rimpi waters, which would appear similar to the solutions under discussion. The present author, from approximate redox titrations of the sample solutions, found about 1×10^{-3} equivalent of rapidly oxidizable material per litre. Taking the values 1×10^{-4} to 1×10^{-3} mol./litre as very probable limits for $c_{Fe^{++}}$ in a soil solution in an anaerobic environment and substituting these values for $a_{Fe^{++}}$ in (3) (assuming $-\log f_{Fe^{++}} = 0{\cdot}25$, see further) gives

$$E_h = (1{\cdot}28 \pm 0{\cdot}03) - 3 \times 2{\cdot}303 \frac{RT}{F} \text{pH}. \qquad (4)$$

Thus for quite considerable changes in $a_{Fe^{++}}$, (1) a plot of E_h against pH should give a near straight line; (2) the slope of the plot should be $-3 \times 2{\cdot}303 \frac{RT}{F}$. This is three times the slope often used to calculate change of E_h with pH in the soil.

Belcher, Gibbons, and West, in a study of the effect of the E.D.T.A. complexing agent on the E_h of the $Fe^{+++} \rightleftharpoons Fe^{++}$ system, give an E_h/pH slope of about −0·150 volts after $Fe(OH)_3$ has started precipitating.

Mlle Bézier, in studies of ferric complexes and ferric solutions practically devoid of ferrous ions, finds a straight line E_h/pH relationship after ferric hydroxide has started precipitating and shows a slope of about −0·160 volts.

Taking her empirical equation

$$E_h = 1{\cdot}01 + 0{\cdot}06 \log(c_{Fe^{+++}}),$$

and substituting for $(c_{Fe^{+++}})$, gives

$$E_h = 1{\cdot}37 - 0{\cdot}18 \text{ pH}.$$

This shows that the E_0 for this system is, in a pure experimental solution, in near accord with equation (4) and, above all, that the E_0 value is such as is required for the system to function in a reduced soil since, for soil pH values, it gives E_h levels comparable to those of a reduced soil.

This system, if it does function in the soil and, if it does control the E_h of the soil solution by equation (3), may be written:

$$Fe(OH)_3 \rightleftharpoons Fe^{+++} \rightleftharpoons Fe^{++} \begin{cases} \rightleftharpoons Fe^{++}\text{—soil exchange} \\ \rightleftharpoons Fe^{II}-R_1 \\ \rightleftharpoons Fe^{II}-R_2 \end{cases}$$

There are, therefore, large reserves of both the oxidized and the reduced forms and the system will be well poised. $Fe^{II}-R_1$, $Fe^{II}-R_2$ will be organic ferrous complex compounds postulated by Bloomfield and others.

Plots of E_h against pH from the experimental samples

From curves such as Fig. 1 and Fig. 2, for a variety of samples, E_h was plotted against pH. The plots start from the time of the peak in period B or from 1 day after the onset of anaerobic conditions, depending on the

TABLE 1

Treatment	Sample + 250 ml. water	Number of pairs of observations	Constant term		Slope		Correlation coefficient
			a	*s.e.a*	*b*	*s.e.b*	
A	30 g. soil + 5 g. roots	30	1·39	0·11	0·192	0·018	0·897
	30 g. soil + 5 g. grass	30	1·04	0·13	0·143	0·021	0·792
	30 g. soil only	32	1·77	0·23	0·227	0·037	0·743
B	30 g. soil only	34	1·25	0·10	0·161	0·015	0·882
	30 g. soil + 5 g. roots	30	1·04	0·11	0·140	0·016	0·846
	30 g. soil + 5 g. roots	29	0·91	0·11	0·120	0·017	0·803
	30 g. soil + 1 g. roots	30	1·38	0·07	0·183	0·010	0·958
	30 g. soil + 1 g. roots	30	1·37	0·07	0·182	0·010	0·961
C	30 g. soil + 0·1 g. roots	9	1·36	0·08	0·182	0·013	0·983
	30 g. soil + 0·05 g. roots	9	1·41	0·12	0·190	0·018	0·971
	30 g. soil + 1 g. grass	9	1·12	0·07	0·150	0·011	0·982
	30 g. soil + 5 g. grass	17	1·02	0·07	0·142	0·012	0·952
	30 g. soil + 5 g. grass	16	1·00	0·11	0·137	0·018	0·896

Table 1 gives the results obtained by fitting a straight-line relationship of the form

$$E_h = a - b(\text{pH})$$

to the results obtained from a series of thirteen experiments. The values of a and b are tabulated, together with their standard errors. In every case both a and b are very much larger than their standard errors (Student's t-test gives a significance level of less than 0·001 per cent.) and the straight-line regression accounts for by far the greater part of the experimental variation. It can be concluded that a straight line provides a satisfactory fit to the experimental results.

Treatment A. Initial anaerobic conditions 16·5 days, followed by aeration 8·5 days (no observations recorded), followed by second anaerobic period 4·5 days.

Treatment B. Initial anaerobic conditions 21 days, followed by aeration for 13 days (no observations recorded), followed by second anaerobic period of 12 days.

Treatment C. Initial anaerobic period for 21 days only.

shape of the first part of the curve, when it is assumed that the systems of higher E_0 have established themselves. The results are set out in Table 1 and a typical plot is shown in Fig. 3. Each of the plots shows a good straight-line relationship and there is some agreement with equation (3), which is support for the suggested mechanism being correct.

Fig. 4 shows the E_h/pH relationships for (*a*) 5 g. roots+250 ml. water; (*b*) 5 g. roots+250 ml. water+either solid ferric hydroxide or the compound coated on acid washed sand (the two results are combined). In both cases the points are for an initial anaerobic submergence of 21 days. The results are inconclusive but it can be seen that the points for (*a*) lie well below the theoretical lines from equation (3), whilst the points for (*b*) lie much closer to the theoretical lines. This is some additional support for the proposed role of iron.

The Fe^{II} contents of the above soil solutions were not determined. Work (unpublished) on similar samples of Sierra Leone rice soils has

given $c_{Fe^{II}}$ about equal to 5×10^{-4} for most samples. The conductivities of these soil solutions varies a great deal but in period C it may be put at about 10^{-3} mhos/cm.[2] The ionic strength, assuming all the ions divalent, will be about 2×10^{-2}, giving $-\log f_{Fe^{++}} = 0{\cdot}25$ and hence $a_{Fe^{++}}$

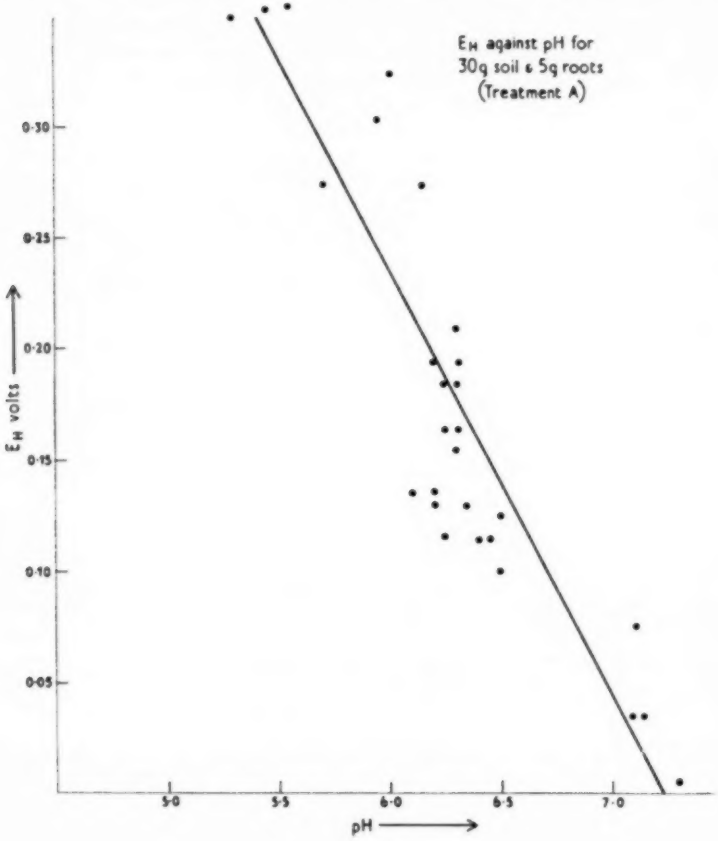

FIG. 3

very approximately equal to 3×10^{-4}. This shows some agreement with the equation (4).

The results suggest that $3 \times 2{\cdot}303 \frac{RT}{F}$ pH is the correct term for adjusting for pH changes the E_h values of submerged soils. However, since field conditions may not exactly correspond with pot conditions, it would seem better invariably to quote both E_h and pH values as measured and to include a third figure for the adjusted E_h if necessary, whatever factor be used for the adjustment.

In a further paper the author hopes to use equation (4) to define more precisely the terms 'oxidizing conditions', and 'reducing conditions' as they are used with reference to paddy soils.

Equation (3), if valid, may also show the importance of pH changes

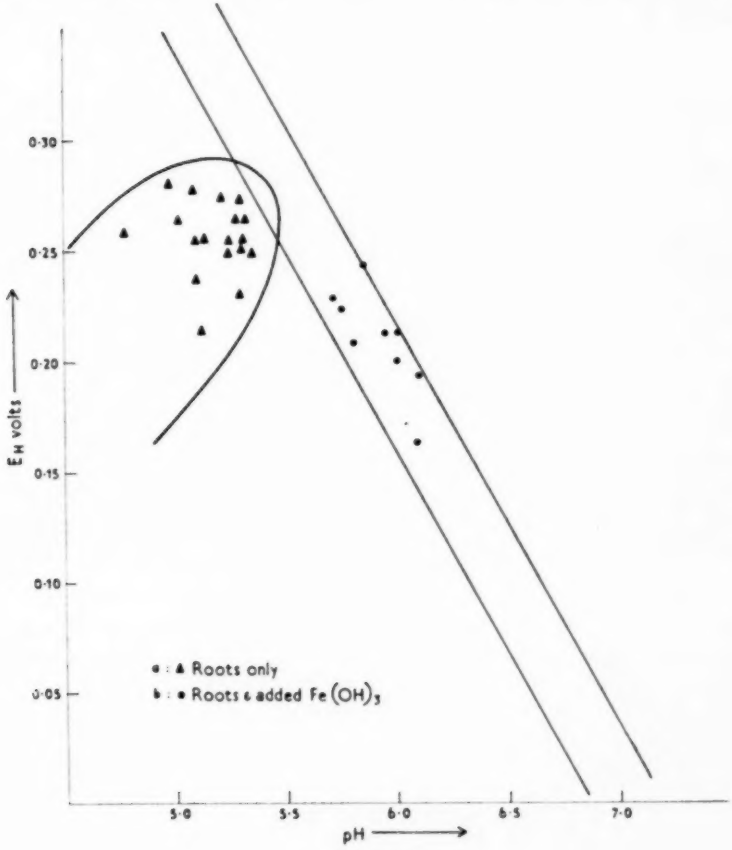

FIG. 4

when considering the movement and precipitation of iron in aerated soils. At pH 5 ferrous compounds may be quite safe from oxidation because the ferrous iron with which they are in equilibrium in the soil solution will not be oxidized until the E_h rises above about 300 mV, but at pH 7 iron will begin precipitating if the E_h is above about 50 mV.

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THE EFFECT OF pH ON THE WET STRENGTH OF SOIL CRUMBS

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Summary

The clay-clay attractive forces were greater in crumbs from acid soils than crumbs from similar soils but containing free $CaCO_3$. This has two causes: (*a*) positive charges on the edge faces of the clay crystals; (*b*) exchangeable trivalent cations on the clay. Using the improved sodium-saturation method these two causes were distinguished by measuring the reduction in the strength of the crumbs by (*a*) raising the pH of the percolating NaCl to 7·4 with para-nitrophenol buffer, and (*b*) preliminary NaCl-HCl leaching. The effect of trivalent cations was dominant in very acid soils where Al^{+++} can exist in the soil solution. The soil conditioner 'Flotal' strengthens soil crumbs, initially at least, by substituting Fe^{+++} ions on the exchange complex. No evidence was found for cementing by precipitated $Al(OH)_3$ or $Fe(OH)_3$.

The same concentration of $CaCl_2$, 6×10^{-3} M was required to flocculate suspensions of moderately acid surface soils both at the natural pH of the soil and after buffering the suspensions to pH 7·4. However a Ca-illite and an acid subsoil (no organic matter) flocculated at a $CaCl_2$ concentration of 3×10^{-4} M at pH 5. Thus there appears to be sufficient organic matter present in normal cultivated acid soils to neutralize the positive charges on the edges of any clay particles dispersed from the crumbs.

It is suggested that, although liming an acid soil decreases the attractive forces between clay particles within soil crumbs, the presence of free $CaCO_3$ in the soil helps to maintain a sufficiently high concentration of electrolyte in the soil solution to reflocculate dispersed clay and so keep drainage waters clear.

1. *Introduction*

It was thought at one time that because calcium salts are very effective flocculants of soil colloids, liming should increase the cohesion of soil crumbs by improving the flocculation of the clay in the crumbs. Neither Baver (1928, 1929) nor Kappen (1931) detected any appreciable increase in crumb stability with increasing calcium saturation (excluding soils containing exchangeable sodium). Peele (1936, 1937, 1938) found that the addition of calcium carbonate to heavy clay soils actually decreased the permeability of columns of these soils to water and decreased the percentage of water-stable aggregates. When organic matter (ground Lespedeza hay, matured for 3 months) was added to Cecil clay there was an increase in permeability of the clay, but when lime and organic matter were added together the lime more than nullified the favourable effect of the organic matter and the soil permeability decreased. A similar result was obtained by Rost and Rowles (1940) who measured crumb stability by the degree of dispersion after end-over-end shaking of limed and unlimed soil crumbs. Childs (1942), using the moisture characteristic method, found that soil crumbs from the lower Lias were less stable to wetting and drying than soils of the same clay content from

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the acid upper Lias. Russell and Basinski (1954), using a wet-sieving technique, observed a slight reduction in the cohesion of clay soils on adding calcium salts.

It can therefore be inferred that for an acid soil which has no sodium on the exchange complex, raising the pH by the addition of lime does not increase the stability of the soil crumbs.

There appear to be three ways in which attractive forces between clay particles might be greater under acid conditions.

(*a*) An electrostatic attractive force between the positive edges and negative faces of the clay crystals.

Schofield and Samson (1954) showed that the edge faces of kaolinite crystals can become positively charged in solution, the amount of positive charge increasing as the pH of the solution is lowered. Similar groups are present on the edge faces of montmorillonite and illite so that it would be expected that these too could become positively charged (Emerson, 1954).

(*b*) The presence of exchangeable trivalent ions (Al^{+++} or Fe^{+++}).

For homoionic clays in neutral solutions of the corresponding chlorides the concentration of salt required for flocculation is known to decrease sharply with increasing valency of the exchangeable cation on the clay. This implies that the attractive force between clay crystals increases with the valency of cation on the clay.

(*c*) The cementing action of precipitated sesquioxides.

There is no direct evidence that soil crumbs may be held together by a sesquioxide coating, although it is presumed to happen in lateritic soils, iron being the cementing agent.

An increase in the attractive forces between the clay particles should also assist in the reflocculation of any clay which becomes dispersed from the soil crumbs. However, once the clay is in suspension, the positive charges on the edge faces of the clay crystals could be neutralized by absorption of dissolved organic matter. This would correspondingly increase the amount of electrolyte required in the soil solution before reflocculation could occur.

To study these possible effects, the sodium-saturation technique (Dettmann and Emerson, 1959) has been extended to compare the wet strength of soil crumbs at different pH, after pretreatments designed by Schofield (1949) to remove any exchangeable aluminium ions. A similar test has been used to measure the resistance to dispersion of pure clays as a function of pH and of added ferric and aluminium salts. The variation with pH of the concentration of Ca^{++} ions required to flocculate suspensions of the acid soils and clays has also been investigated.

2. *Experimental Material*

Pure clay

Illite—the separated clay fraction of Willalooka subsoil, supplied by C.S.I.R.O., Australia. X-ray analysis indicates that the fraction $< 2\mu$ is 85 per cent. illite and 15 per cent. kaolin.

Soils and soil clays

The Rothamsted soils used (0–4 in.) were mineralogically the same (60 per cent. mica-type minerals, 40 per cent. kaolinite, and a little vermiculite), but differed considerably in pH and management history (Table 1). The underlying subsoil from a reclaimed opencast-coal site in Staffordshire was also used (Wagonwheel).

TABLE 1

Mechanical Analyses and pH (in M/100 $CaCl_2$*) of the Soils Used*

Soil	*Coarse sand*	*Fine sand*	*Silt*	*Clay*	*Carbonates*	*pH*
Barnfield . . .	6	37	21	29	0·5	7·2
Broadbalk Acid Headland	6	41	25	19	0·8	3·7
Hoos New Soil Structure Experiment . .	7	48	23	15	..	6·1
Hoos Exhaustion Land .					..	5·3

Chemicals

The chemicals used were of A.R. grade, except for 'flotal' (a soil conditioner), the composition of which is 85 per cent. ferric-ammonium alum, 3 per cent. total nitrogen, and 10 per cent. organic matter (peat).

Preparation of the clay

After treatment with 40-volume H_2O_2, the fraction $< 2\mu$ was separated by sedimentation, flocculated with N NaCl, and then centrifuged and decanted from N NaCl + 10^{-3} N HCl several times to saturate the clay with sodium and displace any exchangeable Al^{+++}. The clay was then brought into suspension and dialysed in cellulose casings against distilled water in which the pH was adjusted to 7·5–8·0 with a few drops of dilute NaOH. The chloride-free, deflocculated clay was made up into suspensions of known concentration. Fe^{+++} and Al^{+++} illites were obtained by adding aliquots of solutions of $[Fe_2(SO_4)_3.(NH_4)_2SO_4.24H_2O\cdot]$, $FeCl_3$, $[Al_2(SO_4)_3.(NH_4)_2SO_4.24H_2O]$, and 'flotal' to the Na-illite.

Preparation of synthetic soil crumbs

Willalooka subsoil and Barnfield 80 were ground in a mortar and the material passing a 40-mesh sieve was mixed with the Fe^{+++} or Al^{+++} solutions, or 'flotal'. Sufficient distilled water was added to make the soil workable. After mixing, the soil was forced through a 3-mm. sieve and the resultant synthetic crumbs dried at 25° C.

3. *Experimental*

(*a*) *The resistance to dispersion of the crumbs*

The sieved 1–2-mm. fraction of the soils was subjected to the modified sodium-saturation test (Dettmann and Emerson, 1959), first using 0·05 N NaCl. A second test was made with NaCl buffered to pH 7·4

with half-neutralized para-nitro-phenol. This buffer was chosen because its dissociation constant, 7·4, is close to the pH in 10^{-2} M $CaCl_2$ of a soil in equilibrium with $CaCO_3$ at a normal atmospheric CO_2 concentration (7·6 at 0·03 per cent. CO_2). The solution used was $4{\cdot}5 \times 10^{-2}$ N NaCl + 10^{-2} N para-nitro-phenol + 5×10^{-3} N NaOH. This had the same Na^+ concentration as the unbuffered NaCl, and contained the lowest concentration of para-nitro-phenol needed to maintain the pH of the leachate from the soil crumbs above 7·0.

TABLE 2

The Permeability of 1–2-mm. Soil Crumbs after Percolation with (a) 0·05 N NaCl, (b) NaCl + pH 7·4 Buffer (Total $Na^+ = 0{\cdot}05$ N*), expressed as a fraction of their Initial Permeability*

Soil	*Barnfield 80*	*Barnfield 2A*	*Barnfield 2N*	*Wagonwheel*	*Hoos Exhaustion*	*Broadbalk Headland (acid)*
pH . .	7·2	7·2	7·2	5·3	5·3	3·7
K_2/K_1%(*a*)	5	11	9	29	90	100
K_2/K_1%(*b*)	5	4	5	4	40	100

The acid soils were chosen on the basis of their long history of arable cropping, so that there would be a negligible contribution by organic matter to the attractive forces between the clay particles in crumbs from these soils. This enabled a comparison to be made between these crumbs and crumbs from Barnfield 80 with a similar history. The results for the manured Barnfield plots 2A and 2N are included to show that there is a slight interaction between the para-nitro-phenol ion and the soil, that makes the use of this buffer unsuitable as a general method of eliminating the effect of pH on crumb strength. However, this effect is small compared with the reduction in the wet strength of Hoos Exhaustion and Wagonwheel soil crumbs on raising the pH of the crumbs to 7·4. This treatment had no measurable effect on the strength of the very acid Broadbalk crumbs.

(*b*) *The effect of acid leaching on the dispersion of soil crumbs*

Sieved 1–2-mm. air-dry samples of soil crumbs from Broadbalk Headland (acid) and Hoos Exhaustion Land were packed into permeameters and wetted at 8 cm. of water suction with 0·05 N NaCl, and the rate of discharge of electrolyte through the crumb bed (permeability K_1) measured as in the sodium-saturation test. The soil crumbs were then flushed with electrolyte (*a*) at pH 3 using 0·5 N NaCl with 10^{-3} N HCl; or (*b*) at pH 2·3 using 0·5 N NaCl with 5×10^{-3} N HCl; or (*c*) using 0·5 N NaCl without addition. The Fe^{+++} and Al^{+++} present in the equilibrium leachates in contact with the soil crumbs were measured colorimetrically—the Fe^{+++} with NH_4CNS, and the Al^{+++} with aluminon every 24 hours, and flushing was continued at the rate of 250 ml. in 24 hours through each permeameter until the Fe^{+++} and Al^{+++} concentrations approached constant values after 7 days. The pH of

the leachates was checked (with a glass electrode and calomel half cell) and it was found that the pH of the soil crumbs was maintained at that of the percolating acid electrolyte. After this leaching process the soil crumbs were flushed with 0·5 N NaCl to remove the HCl remaining in the permeameters and supply tubes, then with 0·05 N NaCl adjusted to pH 7·4 with half-neutralized para-nitro-phenol (3 litres in 24 hours through each permeameter). The rate of discharge of 0·05 N NaCl was measured at the beginning of the 24-hour flushing period through the soil columns (permeability K_2) and at the end of this period (permeability K_3), from which K_2/K_1 and K_3/K_1 shown in Table 3 were calculated.

TABLE 3

Soil	K_2/K_1%	K_3/K_1%	*Final equilibrium conc.* ($N \times 10^{-5}$) Al^{+++}	Fe^{+++}
		Treatment (a)		
Hoos Exhaustion	100	5	9·5	2·1
Broadbalk Headland (Acid)	100	19	20·0	3·2
		Treatment (b)		
Hoos Exhaustion	100	3	33	6·3
Broadbalk Headland (Acid)	100	12	33	13·6
		Treatment (c)		
Hoos Exhaustion	100	..	4·0	0·2
Broadbalk Headland (Acid)	100	..	3·2	0·3

As K_1 and K_2 are identical, the pretreatments at pH 2·3 and 3 have not caused any appreciable breakdown in the crumbs, i.e. the geometry of the system is unchanged, so that the use of K_1 (1·26 cm. water sec^{-1} for 1–2-mm. crumbs) is justified for the calculation of K_3/K_1. The low values of K_3/K_1 after the two acid pretreatments show that the attractive forces between the clay particles have been reduced to the level of those in an arable calcareous soil (Table 1). The more acid of the two pretreatments has been slightly more efficient in removing Al^{+++} and Fe^{+++} as judged either by the equilibrium concentrations of these ions or by the lower values of K_3/K_1.

(*c*) *The effect of exchangeable* Al^{+++} *and* Fe^{+++} *on the dispersion of illite and soil crumbs*

Flakes (about 250 mg.) of Na^+, Fe^{+++}, and Al^{+++} illite (prepared on a sintered glass disc and dried over P_2O_5), and treated and untreated synthetic soil crumbs were used for the following tests:

(i) Placed in specimen tubes containing distilled water buffered to pH 7 with para-nitro-phenol, or to pH 9 with barbiturate. The tubes were covered to prevent thermal agitation. After 24 hours the appearance of the clay flake or soil crumb was noted as: unchanged; or swollen but retaining its identity; or dispersed.

(ii) Placed in specimen tubes containing 0·5 N NaCl + 10^{-3} N HCl.

After 24 hours the solution was decanted and lower concentrations of sodium chloride buffered to pH 7 (with para-nitro-phenol) were added. The appearance was noted as in (i) above.

(iii) Placed in specimen tubes containing 0·01 M $CaCl_2$ which was decanted twice—each time at the end of 24 hours—then replaced in 0·5 N NaCl. The NaCl was decanted and distilled water buffered to pH 7 or pH 9 was added to the tubes. Observations were made after 24 hours.

(iv) Na^+-illite, Fe^{+++}-illite, Hoos Exhaustion clay of moderate pH (untreated) and Hoos Exhaustion clay of moderate pH (acid-washed with 0·5 N NaCl + 10^{-3} N HCl several times) were used for determinations of base-exchange capacity. This was done by leaching the sample with neutral ammonium acetate and estimating the NH_4^+ held on the clay by the Kjeldahl method.

Results

Test (i). Illite and soil to which the equivalent of the base-exchange capacity, or more, of Fe^{+++} or Al^{+++} had been added, remained stable in distilled water buffered at pH 7 and 9. Na-illite dispersed in 0·01 N NaCl, and illite to which less than the base-exchange capacity of Fe^{+++} or Al^{+++} had been added also dispersed in 0·01 N NaCl. The stable clay flakes and soil crumbs swelled appreciably in water.

Test (ii). The illite flakes that were stable to distilled water in test (i) did not retain their stability after leaching with 0·5 N NaCl + 10^{-3} N HCl (at pH 3) and subsequent decantation into dilute sodium chloride at pH 7. The deflocculation concentration of the pre-treated clay flakes and soil crumbs after this treatment was the same as that for Na-illite (0·01 N NaCl), and for the untreated soil crumbs.

Test (iii). The Al^{+++} and Fe^{+++} clay flakes and soil crumbs remained stable after decantation from 0·01 M $CaCl_2$, then 0·5 N NaCl and finally distilled water, showing that Ca^{++} ions had not displaced the Al^{+++} or Fe^{+++} ions within the time scale of this experiment.

Test (iv).

TABLE 4

Base Exchange Capacity of Clays

Clay	*b.e.c.* (*m.e.*/100 *g.*)
Na-illite $< 2\mu$	34·1
Fe^{+++}-illite $< 2\mu$ . . .	33·2
Hoos Exhaustion, moderate pH $< 2\mu$ (untreated) .	31·9
Hoos Exhaustion, moderate pH $< 2\mu$ (acid leached)	31·6

Tests (i)–(iii) show that exchangeable Al^{+++} or Fe^{+++} ions present in the soil are not displaced by leaching with strong NaCl or $CaCl_2$ solutions buffered to pH 7·4, but that these trivalent cations may be exchanged for Na^+ ions by washing with NaCl-HCl mixtures. From the measurements of base-exchange capacity it is apparent that neutral ammonium acetate can displace exchangeable trivalent cations (Table 4).

(*d*) *Flocculation of soil suspensions*

Bulk samples of three Rothamsted soils—from Appletree field (permanent pasture), from Stackyard field, and from the Hoos New Soil Structure experiment (normal arable rotation)—and the Wagonwheel soil were leached with 0·01 M $CaCl_2$ to displace any other exchangeable metal cations present, washed free from Cl^- with distilled water, and air dried. A 5-g. sample of soil was placed in each of a series of centrifuge tubes and 25 ml. of 10^{-3} M $CaCl_2$ added. Two tubes were prepared for each of the Rothamsted soils, the first with pH unadjusted, and the second with pH adjusted to 7·5 using half-saturated calcium hydroxide. The soil suspensions were thoroughly shaken on a reciprocating shaker, then lightly centrifuged. If after this treatment the solution was turbid, 0·5-ml. aliquots of 1·0 M $CaCl_2$ were added and the procedure repeated until the supernatant liquid was clear. If the supernatant liquid was clear in 10^{-3} M $CaCl_2$ it was decanted and a lower concentration of calcium chloride added, adjusting the pH as before. After shaking the suspensions, they were again centrifuged and, failing a clear supernatant liquid, 0·5-ml. aliquots of 1·0 M $CaCl_2$ were added until the supernatant liquid cleared—this was taken as the criterion for flocculation. The concentration of calcium chloride in the clear supernatant liquid was determined by measuring its resistance in a calibrated cell using a 1,000 cycles/sec. oscillator and a Wheatstone bridge.

A similar experiment measured the effect on the flocculation concentration of adding sodium alginate of low molecular weight (about 15,000) to the Wagonwheel subsoil.

Results

When the concentration of calcium chloride had been reduced to near the deflocculation concentration of the clay in the suspensions, it was necessary to centrifuge the suspensions for a longer period to obtain a clear supernatant liquid, the volume of which steadily decreased as the deflocculation concentration was approached. Hence the figures given for the flocculation concentration of the soils in Tables 5 and 6 are subject to small uncertainties.

TABLE 5

The Variation with pH in the Concentration of $CaCl_2$ *Required for Flocculating Untreated Soils*

Soil	*pH*	*Flocculating concentration of* $CaCl_2$ ($M \times 10^{-4}$)
Appletree Field	5·4	64
(Permanent grass)	7·6	64
Stackyard	5·4	62
(Normal arable rotation)	7·5	61
Hoos New Soil Structure	6·2	67
(Normal arable rotation)	7·5	68

Table 5 shows that the concentration of $CaCl_2$ required for flocculation

is the same for all the acid Rothamsted surface soils at both the natural pH of the soil and at pH 7·4. This shows that the charge distribution on the clay particles in suspension is the same at both pH values. A similar result was achieved by adding a small quantity of sodium alginate (one-sixth of the base-exchange capacity of the soil) to the Wagonwheel soil, which is a raw subsoil very low in organic matter. It will be noted that the presence of sodium alginate increased the flocculating concentration of $CaCl_2$ by a factor of 10. The flocculating concentration for Ca-illite (Willalooka subsoil extract) was 3×10^{-4} M $CaCl_2$ at pH 5.

TABLE 6

The Variation with pH in the Concentration of $CaCl_2$ *required to flocculate Wagonwheel Soil treated with Sodium Alginate*

pH	% *Alginate* (*by weight*)	*Flocculating concentration of* $CaCl_2$ ($M \times 10^{-4}$)
4·6	0·0	2
	0·1	45
	0·5	50
7·5	0·0	4
	0·1	45
	0·5	46

4. *Discussion*

The results in Table 2 show that where bonding by organic matter is excluded, clay-clay attractive forces are stronger in acid than in calcareous soils. The respective contributions to this of positively charged edges and exchangeable trivalent cations may be distinguished by whether the strength of the crumbs is appreciably decreased after raising the pH of the percolating NaCl solution to 7·4, or only after acid leaching. From Table 2 it is evident that trivalent cations are only important in very acid soils. Raupach (1957) has suggested an upper limit to the pH of 4·9 for the presence of Al^{+++} ions in the soil solution. It is impossible to arrive at a limit from the results here; for the strength of crumbs from Hoos soil (pH 5·3), although decreased when the pH of the percolating NaCl was raised to 7·4, was brought to the level of a calcareous soil crumb only by acid leaching, whereas the strength of Wagonwheel crumbs (natural pH 5·3) was decreased to that of Barnfield crumbs (same clay content) at pH 7·4. No attempt has been made to decide whether it is exchangeable Al^{+++} or Fe^{+++} which is stabilizing the acid Broadbalk soil. It is much more likely to be Al^{+++}, because the first dissociation constant of $Fe(OH)_3$, 37·2, is appreciably higher than that for $Al(OH)_3$, 32·3 (Latimer, 1952).

Attention has been concentrated on the possible effect of trivalent cations, as other monovalent ions present on the exchange complex (specifically in moderately acid soils) such as H^+ or $Al_3(OH)_8^+$ (Raupach, 1957) would be expected to exchange for Na^+ ions on percolating the soil with N NaCl. Norrish (1954), for example, has shown that H-montmorillonite swells initially to the same extent in HCl solutions as

Na-montmorillonite in NaCl solutions of the same concentration, before reversion of the H-montmorillonite to a H-Al-montmorillonite.

The ability of neutral ammonium acetate to displace exchangeable trivalent cations was not realized until after the main experiments had been completed. In this process the NH_4^+ ion itself can be of little importance, because a strong solution of $CaCl_2$ involving a divalent cation was ineffective. There remains the acetate anion which is known to form complexes with metals much more effectively than chlorides (Bailar, 1956).

The possibility, mentioned in paragraph 1, of acid soil crumbs being stabilized by precipitated $Al(OH)_3$ or $Fe(OH)_3$ will now be considered. Air-dry crumbs from all the acid soils whose strength was measured by the sodium method, and synthetic crumbs treated with Al^{3+} or Fe^{3+} salts, were observed to slake in the same way as those of corresponding calcareous soils. This implies that the clay in the acid soil rapidly takes up its normal 'crystalline' water-layers (Dettmann, 1958) in the same way as Al-montmorillonite (Norrish, 1954), so that there is no 'cementing' between the faces of the clay particles. Moreover, the edge faces of the swelling clay aggregates cannot be linked either, otherwise breakdown into discrete particles would not occur. There is no evidence, therefore, for binding by sesquioxides in the acid soils investigated.

The flocculation experiments show that clay shaken into suspension from acid soil crumbs containing organic matter behaves in the same way as an acid subsoil to which sodium alginate had been added. This could happen either because organic matter in solution neutralizes the charge on the edge faces of the clay crystals, or because the shaking procedure breaks organic-matter bonds linking the clay aggregates in the crumbs. The net result is that a high concentration of Ca^{++} ions is required to reflocculate the clay. The presence of free $CaCO_3$ will assist this, for with an average CO_2 concentration in the soil atmosphere (0·1 per cent.) the equilibrium Ca^{++} concentration will be 3×10^{-3} M, for a soil at pH 7·6. This is of particular importance for mole drainage where silting up is a cause of failure.

Nicholson (1942) showed that clay formations containing considerable quantities of free calcium carbonate, such as Gault clay from the Cambridge University Farm, are particularly suitable for mole draining. In a drainage experiment on a non-calcareous soil, Childs (1943) observed that the amount of suspended material in the drainage water from limed plots was only one-third of that from unlimed plots.

Keen and Haines (1925) found a reduced draught of tillage implements in soils containing free calcium carbonate, reflecting the reduced wet strength of the soil crumbs and weaker crust.

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MEASUREMENT OF SOIL ANISOTROPY WITH PIEZOMETERS

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Summary

A detailed investigation of soil anisotropy on a small test area is reported. Measurements were made with piezometers of various diameters. The method employed involves two measurements of hydraulic conductivity in a single piezometer. In addition, transmission rates were determined on horizontal and vertical undisturbed core samples.

The results show the vertical hydraulic conductivity to be highly variable and dependent on the depth below the soil surface. The horizontal hydraulic conductivity is less variable. Results of anisotropy calculations from piezometer measurements show a dependence on the dimensions of the cavity below the piezometer, the large piezometers gave anistropy ratios < 1, the small piezometers generally > 1.

The dependence of test results on cavity dimensions is explained by the dependence of the vertical hydraulic conductivity on depth below the soil surface. Taking account of the inhomogeneous nature of the soil in the conventional analysis of anisotropy yields a similar dependence on cavity dimensions as was found from the field data. It is concluded that anisotropy calculations may lead to erroneous conclusions when applied to conditions in which the assumptions implicit in the theory are not approximately fulfilled.

The usefulness of the methods employed in this investigation is that valuable data regarding soil variability have been obtained. This variability was not apparent in a previous study with the augerhole method.

Introduction

THE hydraulic conductivity at a point of an anisotropic soil varies with direction. The effect of the factors active in soil formation is such that, in most soils, the difference in hydraulic conductivity will be greatest between the horizontal and vertical directions. For example, distinct horizontal stratification may result from the process of sedimentation. Such processes will generally produce a higher horizontal than vertical hydraulic conductivity. The opposite effect may result from the development of deep root systems, worm holes, or vertical shrinkage planes arising from the drying of certain clay soils. In the following it will be assumed that the principal directions of anisotropy (Maasland, 1957, p. 218) coincide with the horizontal and vertical.

Maasland (1957, pp. 240–6) discusses the factors which cause anisotropy, and lists from the literature anisotropy ratios, obtained mainly from measurements on core samples. This discussion shows that the horizontal conductivity usually exceeds the vertical. Childs *et al.* (1957), using a procedure combining the two-well method of Childs (1952) and the tube method of Kirkham (1945), study anisotropy by 'in place' measurements of hydraulic conductivity. They report that half the sites investigated exhibited anisotropy and in a few cases the vertical hydraulic conductivity exceeded the horizontal. Childs *et al.* emphasize in their

discussion the significance of sample size on the measurement results. This factor seems highly relevant with respect to the present work also.

The present study was designed to assess the degree of anisotropy of soils in the Murrumbidgee Irrigation Areas where an extensive drainage project is now being undertaken. Although the objective of the study has not been fully realized, significant conclusions have been reached concerning the value of 'in place' hydraulic conductivity measurements for evaluating the degree of anisotropy. The method employed, involving two piezometer measurements at one location (Maasland, 1957, pp. 275–83), differentiates between the horizontal and vertical hydraulic conductivity components of an ideal anisotropic system. This method, being relatively simple, allows replication and therefore estimation of the degree of variation. Details of the field work and of the analysis are described below.

Analysis of Inflow into Piezometers in Anisotropic Soil

Maasland (1957, pp. 265–83) gives a full account of the theory of flow into cavities in isotropic and anisotropic soil. A brief resumé of the theory and its underlying assumptions is given because frequent reference to it appears necessary in the subsequent discussion of field measurements. An example of computing anisotropy from field measurements is included in this section.

The general formula for flow into piezometer cavities is (Kirkham, 1945; Maasland, 1957, pp. 265–76):

$$k = \frac{\pi R^2 \ln(y_1/y_2)}{S(t_2 - t_1)} \tag{1}$$

where k is the hydraulic conductivity, R the inside radius of the piezometer, y_1, y_2, &c., the hydraulic head at times t_1, t_2, &c., and S is a constant for a given flow geometry.

For isotropic soils Maasland (1957, p. 266) gives the following functional expression:

$$S/D = f(d/D, w/D, s/D) \tag{2}$$

which for piezometers in an infinite medium becomes

$$S/D = f(w/D) \tag{3}$$

where (see Fig. 1) d is the depth of the bottom of the tube below the water-table, D the diameter of the cavity, w the length of the cavity, and d the depth of impermeable layer below the bottom of the cavity.

In the analysis of field measurements the s/D values of Luthin and Kirkham (1949), obtained with an electric analogue model for values of w/D between 0 and 8, have been used (Fig. 2). For larger values of w/D the approximate formula (Hvorslev, 1951, p. 31, case 8; Maasland, 1957, p. 272)

$$S/D = \frac{2\pi(w/D)}{\ln 2w/D} \tag{4}$$

was used.

For the type of anisotropy discussed, flow is assumed to occur in a homogeneous, anisotropic soil in which the hydraulic conductivity is a

function of direction, but not of coordinates. It is further assumed that the hydraulic conductivity does not vary in the horizontal plane. This anisotropic space is changed into an equivalent isotropic space by a change in scale of the coordinates, viz.

$$x' = x, \quad y' = y \quad \text{and} \quad z' = (k_h/k_v)^{\frac{1}{2}}z,$$

where x and y are the coordinates in the horizontal plane and z is the vertical coordinate.

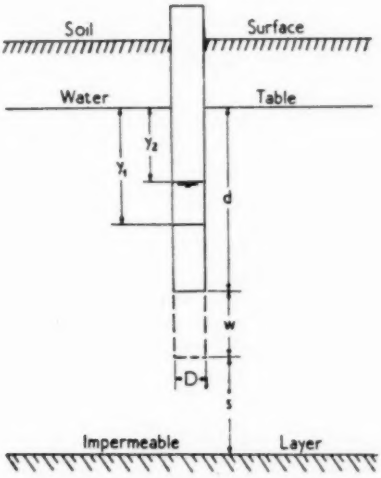

FIG. 1. Piezometer in isotropic soil.

Maasland (1957, p. 276) gives for the rate of inflow into piezometers in anisotropic soil:

$$(k_h k_v)^{\frac{1}{2}} = \frac{\pi R^2 \ln(y_1/y_2)}{S_a(t_2 - t_1)}, \tag{5}$$

where the subscript a of S_a denotes the condition of anisotropy. For a piezometer in an infinite medium with cavity length w and diameter D, the factor S_a/D is given by

$$S_a/D = f[(k_h/k_v)^{\frac{1}{2}} w/D]. \tag{6}$$

In the case where $w = 0$ the cavity shape in the transformed space remains unaltered and thus we may here use the value $S/D = 2{\cdot}45$ (from Luthin and Kirkham, 1949; see Maasland, 1957, p. 269) for S_a/D in (5). A measurement with $w = 0$ therefore gives $(k_h k_v)^{\frac{1}{2}}$. If next a measurement is made with a cavity of length w below the base of the piezometer, without altering its position in the soil, we can find the value of S_a/D from (5) since the value of $(k_h k_v)^{\frac{1}{2}}$ is known from the first measurement and all other quantities (except S_a) are known or measured during the second measurement. This S_a/D value is one found (from Fig. 2) for a definite value of w'/D (cavity dimensions in the transformed

isotropic space). The relationship between w/D and w'/D may be deduced from (3) and (6), from which we find

$$\frac{w'/D}{w/D} = w'/w = (k_h/k_v)^{\frac{1}{2}}. \tag{7}$$

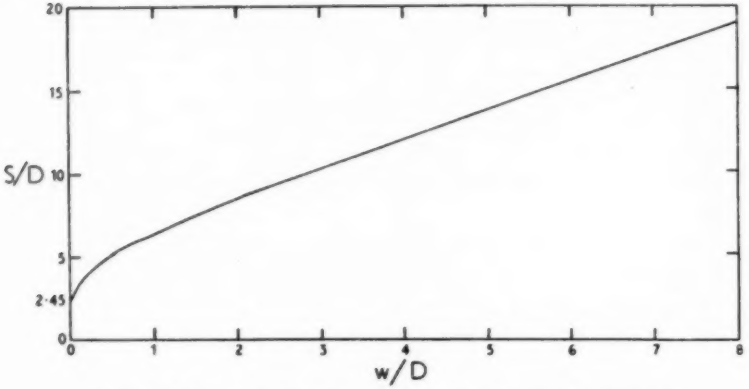

FIG. 2. $S/D = f(w/D)$; for anisotropic soil the coordinates are S_a/D and $w'/D = (k_h/k_v)^{\frac{1}{2}} w/D$.

Both the product and the quotient of k_h and k_v are now known and thus the two components can be separated. For example, assume the value of $(k_h k_v)^{\frac{1}{2}}$, measured with $w = 0$ and a piezometer with $D = 0{\cdot}4$ ft., to be 2 ft./day. Next a cavity of length $w = 0{\cdot}8$ ft. below the piezometer gives $S_a/D = 12{\cdot}2$. From Fig. 2 it is seen that this corresponds to a value of $w'/D = 4$. The actual value of $w/D = 0{\cdot}8/0{\cdot}4 = 2$, therefore from (7) $(k_h/k_v)^{\frac{1}{2}} = 2$. Thus $k_h/k_v = 4$ and $k_h k_v = 4$, from which follows $k_h = 4$ ft./day and $k_v = 1$ ft./day.

Experimental Procedure

The standard piezometer used consisted of a 5 or 6 ft. long, 16 gauge, galvanized iron liner of 0·4 ft. internal diameter. The liner was reinforced at the top with a 6-in. long, 16 gauge galvanized iron sleeve and a 2-in. by $\frac{3}{8}$-in. steel ring. At the lower end it was bevelled on the outside to provide a sharp cutting end. In addition piezometers of 0·129-ft. diameter were used. These were of heavier gauge iron and were not reinforced at the top. The piezometers were installed by alternate driving and augering. A flat bottom at the base of the piezometers was obtained by using a specially designed auger (Childs *et al.*, 1957) at the last stage of installation.

Anisotropy ratios were also calculated from measurements in a number of large diameter cylindrical wells with a well diameter of 3·75 ft. Only the part of the well below the watertable was lined with a reinforced sheet of 16 gauge galvanized iron, bolted together and waterproofed with a strip of rubber at the joint. After use in one well the bolts were

unscrewed so that the liner could be folded and used again in the next well. This liner was installed by slowly driving it into a hole of slightly smaller diameter.

Visual inspection of the seal in the large wells showed that this method of installation was quite effective. Since the smaller piezometers were installed in an essentially identical manner it was assumed that they were also effectively sealed.

After the water-level in a piezometer had reached the equilibrium position, this level was suddenly lowered; in the case of the smaller piezometer by means of a bail bucket and in the case of the large wells with a 2½-in., petrol-driven, pump. The subsequent rate of return flow was measured with a reel-type electric probe.

The first measurement, giving $(k_h k_v)^{\frac{1}{2}}$, was made without a cavity below the piezometer or well liners (this method is known as the tube-method). Subsequently, a cavity was excavated with diameter equal to the piezometer or well diameter. Cavity lengths (w) for the piezometers varied from 0·4 to 0·8 ft., for the wells from 1·0 to 1·5 ft. The second measurement, giving S_a, was then made. Thus the value for $(k_h k_v)^{\frac{1}{2}}$ was always obtained at the top of the cavity.

Horizontal and vertical undisturbed core samples of 3·37 in. diameter and 3·5 in. long, were taken from a large pit 6 ft. by 6 ft. and 8 ft. deep. In the laboratory these samples were saturated and placed in a constant head permeameter to obtain transmission rates. Local, saline, ground-water was used as the permeating fluid.

Site Description

Data reported in this investigation were obtained from a relatively small area (less than 1 acre) located on the Research Station farm. Although this area includes two soil types, Hanwood loam and Yandera loam (Taylor and Hooper, 1938), the deep subsoils of the two types are similar. The subsoil consists of riverine micaceous sandy clay loam to clay loam with little or no structural development. Taylor and Hooper (1938, p. 27) observe that this subsoil (from 4 ft. downwards) sometimes consists of alternating bands of clay loam and sandy clay loam. Mechanical analyses were made of soil samples, taken on a close grid (transects I and II, Fig. 3) between 4·5 and 6·5 ft. over the whole length of the test area. The amount of clay plus silt in the samples varied from 25 to 40 per cent. The variation mostly appeared at random, but was sometimes, as stated above, more pronounced in the vertical direction.

All measurements reported were made in the stratum between 4·5 and 6·5 ft. below the soil surface. The first series of measurements was made with 0·4 ft. diameter piezometers on two transects, I and II (Fig. 3) over the test area, giving a total of 131 estimates of horizontal and vertical hydraulic conductivity. Subsequently, six large wells, numbered A–F, were dug alongside one of the transects, each of these being surrounded by eight piezometers of 0·40 ft. diameter and these in turn by an equal number of piezometers of 0·129 ft. diameter. The distance between individual piezometer locations everywhere was from

6 to 8 ft. apart. Fig. 3 shows the location of the various test sites within the experimental area.

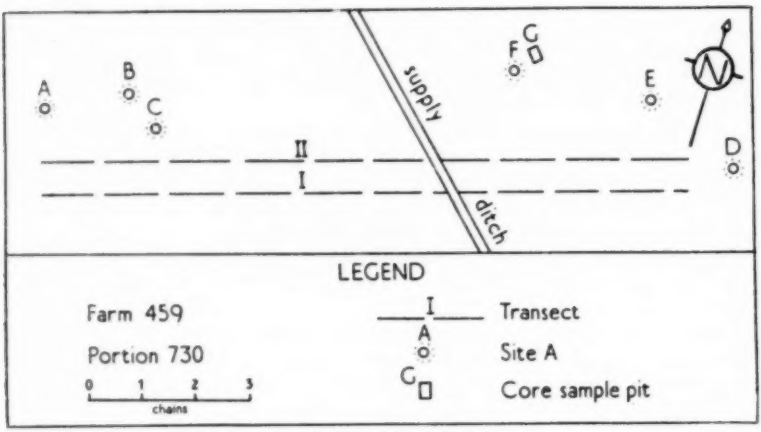

FIG. 3. Map of the test area.

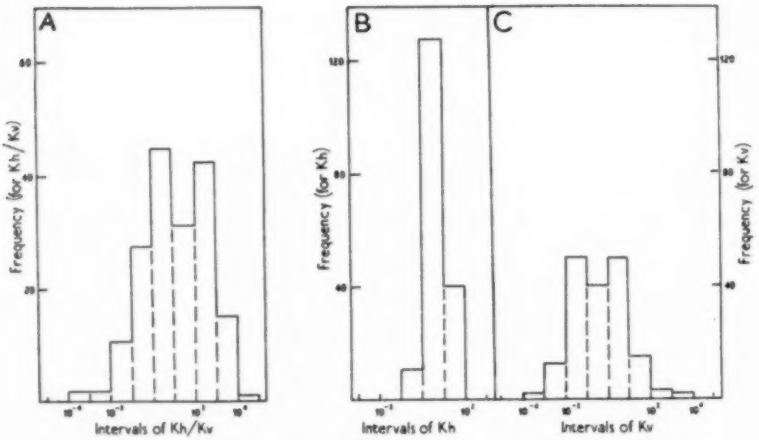

FIG. 4. Frequency distribution of k_h/k_v, k_h and k_v, measured with 0·4 ft. diameter piezometers.

Results

The results of measurements made with the 0·4 ft. diameter piezometers are given in Fig. 4. Fig. 4A shows the frequency of occurrence of the anisotropy ratio k_h/k_v within certain intervals, ranging from 10^{-4} to 10^{+5}. A similar distribution, over intervals of hydraulic conductivity, for k_h and k_v is shown in Fig. 4B and C.

Results obtained at sites A–F, with cavity diameters of 0·129 ft., 0·40 ft., and 3·75 ft. are shown in Tables 1, 2, 3, and 4. Table 1 gives the results of measurements made at sites A and B. Sites C–E yielded data of similar variability; full results of these measurements are therefore not presented. Values of $k_{apparent}$ (col. 6) were calculated from the rate of rise in the piezometer with cavity of length w (col. 3), for the assumed condition of isotropy. The variability of $(k_h k_v)^{\frac{1}{2}}$ and k_v in relation to cavity diameter is indicated in Table 2. Average values of k_{app} and k_h are given in Table 3. Using the data from Table 3, overall average values of k_{app} and k_h, obtained with the various size cavities, were calculated and listed in Table 4.

TABLE 1

Results of Measurements of Anisotropy at Sites A and B

Hole no.	*Diameter* $D=2R$ *(ft.)*	*Cavity lengths (ft.)*		$(k_h k_v)^{\frac{1}{2}}$ *(ft./day)*	k_{app} *(ft./day)*	k_h/k_v	k_h *(ft./day)*	k_v *(ft./day)*
A0	3·75	0	0·80	4·35	4·20	0·87	4·05	4·66
A1	0·40	0	0·66	2·35	2·04	0·57	1·77	3·11
A2	0·40	0	0·66	1·87	3·27	8·5	5·45	0·642
A3	0·40	0	0·66	1·32	4·87	93	12·7	0·137
A4	0·40	0	0·66	0·54	3·62	468	11·7	0·025
A5	0·40	0	0·66	2·70	4·17	5·6	6·40	1·14
A6	0·40	0	0·66	1·31	2·38	9·5	4·04	0·426
A7	0·40	0	0·66	0·37	2·85	645	9·39	0·0146
A8	0·40	0	0·66	3·95	4·06	1·1	4·13	3·76
A9	0·129	0	0·63	0·453	11·3	5,580	33·8	0·00606
A10	0·129	0	0·63	0·092	7·4	82,000	26·3	0·000321
A11	0·129	0	0·63	4·47	1·99	0·03885	0·877	22·8
A12	0·129	0	0·64	10·8	3·79	0·0102	1·09	107·0
A13	0·129	0	0·78	3·93	2·17	0·126	1·40	11·1
A14	0·129	0	0·78	10·5	5·01	0·0682	2·74	40·2
A15	0·129	0	0·80	0·185	7·24	14,000	21·9	0·00156
A16	0·129	0	0·80	30·4	12·9	0·042	6·23	148·2
B0	3·75	0	1·00	2·42	1·85	0·09	0·725	8·06
B1	0·40	0	0·78	0·25	2·86	1,600	10·0	0·00625
B2	0·40	0	0·78	0·23	2·70	1,680	9·43	0·00561
B3	0·40	0	0·78	5·89	4·10	0·19	2·56	13·5
B4	0·40	0	0·78	1·46	2·95	11·8	5·01	0·425
B5	0·40	0	0·78	2·27	3·06	3·3	4·12	1·25
B6	0·40	0	0·78	4·81	2·95	0·095	1·48	15·6
B7	0·40	0	0·78	13·2	6·75	0·034	2·44	71·5
B8	0·40	0	0·78	1·75	1·77	1·05	1·79	1·71
B9	0·129	0	0·63	0·353	2·02	152	4·36	0·0287
B10	0·129	0	0·63	0·359	2·20	180	4·82	0·0268
B11	0·129	0	0·63	0·0275	0·37	1,220	0·96	0·000788
B12	0·129	0	0·67	1·10	3·88	43·5	7·25	0·167
B13	0·129	0	0·75	0·12	1·52	1,025	3·84	0·00375
B14	0·129	0	0·77	0·00343	2·16	7,190,000	9·20	0·00000128
B15	0·129	0	0·80	0·281	3·42	900	8·44	0·00938
B16	0·129	0	0·80	1·41	3·42	2·39	3·40	0·588

Trends of k_h and k_v, obtained at site G with horizontal and vertical core samples, over the interval from 4 to 7 ft. below the soil surface are presented in Fig. 5. Each point in the figure represents the geometric average of twelve measurements. These values, although of the same order of magnitude, are generally lower than the conductivities obtained with the piezometer method.

TABLE 2

Variability of $(k_h k_v)^{\frac{1}{2}}$ and k_v at Sites A–F in relation to Cavity Diameter

Cavity diameter (ft.)	$(k_h k_v)^{\frac{1}{2}}$ *variable between (ft./day)*	k_v *variable between (ft./day)*
3·75	1·84–6·66	2·18–17·80
0·40	$3{\cdot}30.10^{-2}$–13·30	$5{\cdot}86.10^{-5}$–$10{\cdot}68.10^{2}$
0·129	$6{\cdot}14.10^{-4}$–42·60	$1{\cdot}29.10^{-7}$–$13{\cdot}20.10^{3}$

TABLE 3

Average Values of k_{app} and k_h at Sites A–F*

Hole no.	*Diameter (ft.)*	k_{app} *(ft./day)*	k_h *(ft./day)*	k_h/k_v
A0	3·75	4·20	4·05	0·87
A1–A8	0·40	3·28	5·88	..
A9–A16	0·129	5·32	5·04	..
B0	3·75	1·85	0·725	0·09
B1–B8	0·40	3·17	3·66	..
B9–B16	0·129	1·90	4·43	..
C0	3·75	5·29	2·49	0·14
C1–C8	0·40	3·96	8·07	..
C9–C16	0·129	4·22	3·40	..
D0	3·75	1·52	0·495	0·051
D1–D8	0·40	1·75	1·82	..
D9–D16	0·129	2·09	9·65	..
E0	3·75	1·77	1·55	0·71
E1–E8	0·40	3·31	1·57	..
E9–E16	0·129	2·14	6·50	..
F0	3·75	2·04	1·23	0·25
F1–F8	0·40	2·58	6·77	..
F9–F16	0·129	4·21	10·10	..

* Geometric averages.

TABLE 4

Effect of the Cavity Dimensions on k_{app} and k_h

w* *(ft.)*	D *(ft.)*	w/D *(ft.)*	d* *(ft.)*	*Depth Piezometer base* (ft.)*	k_{app} *(ft./day)*	k_h *(ft./day)*
1·13	3·75	0·30	1·45	4·90	2·78	1·76
0·80	0·40	2·00	1·45	4·90	3·01	4·63
0·70	0·129	5·43	1·70	5·40	3·31	6·52

* Average values from measurements on sites A–F.

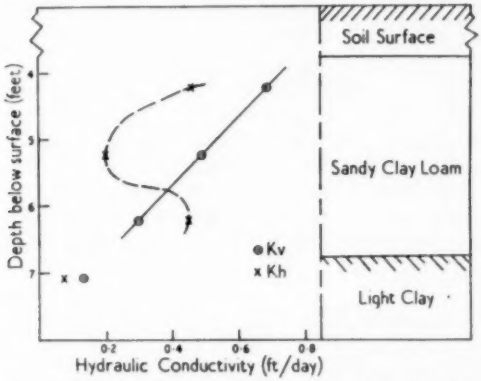

FIG. 5. Trends of k_h and k_v with depth below the soil surface, site G.

Discussion

(*a*) *Analysis of field data*

The results presented in Fig. 4 indicate that the degree of anisotropy over the relatively small test area is highly variable from point to point, apparently due to the highly variable nature of k_v (Fig. 4C). No attempt was made to compute an average value of k_h/k_v from these data, but rather to reduce this variability by increasing the sample size. Since especially k_v appears variable, the diameter of the cavity was increased rather than the cavity length. Also, decreasing the diameter of the cavity should increase the variability of k_v. The data of Table 2 confirm that variability of k_v decreases when the diameter of the cavity becomes greater.

It was observed during the construction of the large wells that fairly large (up to $\frac{1}{8}$ in.) continuous channels exist to a considerable depth below the watertable. Their distribution in the horizontal plane is irregular and their main direction downward. The channels were often found to be coated with a smooth 'skin', which may well be the reason for their permanent existence below the watertable. These downward channels are undoubtedly of importance in contributing towards the variability of k_v.

The variation in k_h is small compared to that of k_v (Fig. 4B and C, Table 1). Similarly k_{app}, which is primarily determined by k_h (Maasland, 1957, p. 279), is less variable than $(k_h k_v)^{\frac{1}{2}}$ (Table 1). Average values, from measurements at sites A–F, are therefore given only for k_{app} and k_h (Tables 3 and 4).

Similar results were obtained at two different locations, approximately 1 and 3 miles from the test area. At the one site the stratum investigated was a slowly permeable, poorly structured clay, at the other there was a permeable, highly structured light clay. The highly variable nature of k_v in relation to k_h therefore does not appear to be peculiar only to the present test area.

Values of $(k_h k_v)^{\frac{1}{2}}$ and k_{app} for the piezometers of 3·75 ft. diameter are

probably on the high side, since (see Table 4) the ratio d/D has only a small value. These large piezometers, therefore, cannot be considered to be installed in an infinite medium and the substitution of equation (3) for equation (2) is not strictly valid. The value of S/D will in that case be somewhat larger (see, for example, Kirkham, 1945, equation 34*a* for the dependence of S/D on d/D). Since generally there is no shallow impermeable layer at the location of the test area, the value of s/D will in most cases be so large that its effect on S/D (equation 2) is negligible. Occasionally, local 'impermeable' layers are found at a higher level in the test area and their presence would reduce the value of S/D (Luthin and Kirkham, 1949).

The trends established with piezometer measurements regarding overall magnitude of the anisotropy ratio k_h/k_v are conflicting. From the distribution of k_h/k_v in Fig. 4A it would appear that the soil is anisotropic with k_h generally larger than k_v (137 out of 180 measurements gave $k_h/k_v > 1$). The trend of k_{app} in Table 4, where the apparent hydraulic conductivity increases as w/D increases, also indicates that this soil is anisotropic with $k_h/k_v > 1$ (see Maasland, 1957, p. 279, table 7). Anisotropy ratios obtained with the 3·75 ft. diameter cavities, however, are all smaller than 1 (Table 3). A surprising result is that k_h shows a dependence on w/D (Table 4). Core sample values of k_h/k_v, over the depth interval of the piezometer measurements (from 4·5 to 6·5 ft. below the surface), indicate that there is no large difference between k_h and k_v at site G (Fig. 5).

The anomalous results obtained with the piezometer method can be explained if it is postulated that k_v decreases sharply with depth below the soil surface. Talsma and Flint (1958) have shown that the overall hydraulic conductivity decreases with depth; in the soil investigated (containing 25–40 per cent. clay plus silt) this decrease would be approximately 10 per cent. for each foot interval (see fig. 2 of Talsma and Flint). The values reported by these authors are apparent conductivities and no attempt was made to assess the relative contribution of k_h and k_v to this decrease.

The core sample values (Fig. 5), which were obtained for this purpose, show that the decrease of k_v with depth at site G is regular and marked. Over the interval between 5 and 6 ft. below the soil surface the decrease of k_v is approximately 40 per cent. as compared with the decrease of 10 per cent. for the apparent hydraulic conductivity. The trend of k_h with depth is irregular at this location, k_h actually increased between 5 and 6 ft. A somewhat heavier textured layer (light clay, see Fig. 5) occurred at 6½ to 7 ft. below the soil surface at site G, resulting in low values for both k_h and k_v at 7·2 ft. depth. This layer is not continuous over the whole test area.

Field observations made during excavations of the sampling pit at site G indicate that this sharp decrease of k_v with depth may be due mainly to the distribution of root channels, which become both smaller in diameter and less numerous with depth. As a similar trend was observed in the large wells (sites A–F), the results at site G are assumed to be valid over the whole test area.

Returning to the discussion of the anomalous results obtained with the small and large piezometers, it may now be explained why a lower value of k_h/k_v was obtained with the large diameter piezometers and why there is a dependence of k_h on w/D. In the conventional analysis of anisotropy (Maasland, 1957, and others), k_v is assumed to be constant with depth. The application of the results of that analysis to measurements in a soil which exhibits physical characteristics different from those assumed in the theory, will obviously lead to erroneous conclusions. The effect on the final answers of the conditions as encountered in this investigation, will be explored in the following paragraphs.

(*b*) *Piezometer measurements in non-homogeneous soil*

It is remembered that the first piezometer measurement was made with a cavity of depth $w = 0$ at the base of the piezometer, and the second had a cavity of depth w greater than zero. The cavity of depth $w > 0$ was dug after the first measurement was completed without changing the position of the piezometer tube. The value $(k_h k_v)^{\frac{1}{2}}$ was calculated from the first measurement and was obtained at a height where k_v was relatively high as compared to the overall k_v for the second measurement because k_v decreases with depth. The second measurement, yielding the product $(k_h k_v)^{\frac{1}{2}} S_a$ in equation (5), is used to calculate S_a by dividing the latter product by the value $(k_h k_v)^{\frac{1}{2}}$ obtained from the first measurement. Since that $(k_h k_v)^{\frac{1}{2}}$ value is too high for the second measurement, the value of S_a so calculated will be relatively too low. Fig. 2 shows that S_a increases monotonically with $w' = w(k_h/k_v)^{\frac{1}{2}}$ so that a low S_a will yield a low value of $(k_h/k_v)^{\frac{1}{2}}$. The large diameter piezometers had a relatively large cavity depth w as compared to the small diameter piezometers (Table 4). The difference between the values of k_v at the top and at the bottom of the cavity becomes greater as w increases and, if the top of the cavity starts at the same depth below land surface in all measurements, the 'equivalent' quotient k_h/k_v will progressively decrease with increasing w. Since the large diameter piezometers had also the largest w, a progressive decrease of (k_h/k_v) should be expected with increasing diameter, as was found from the measurements. A decrease of k_h/k_v would also mean a decrease of k_h if $(k_h k_v)^{\frac{1}{2}}$ is determined at the same depth below land surface for all measurements, and if the factor $S_a = 2{\cdot}45D$ may be used for the first measurement in all piezometers in such a non-homogeneous soil as is here under consideration, an assumption which will not strictly be valid.

Apart from the above considerations there is another reason why k_h/k_v and also k_{app} should decrease if the diameter of the cavity increases. Increasing the diameter of the cavity means that the effective sample size increases. Reeve and Kirkham (1951) define as effective sample size the portion of the soil in which 80 per cent. of the hydraulic head is dissipated. The corresponding equipotential line extends to a greater depth in the case of a cavity of large diameter. Thus an apparent hydraulic conductivity is obtained for a deeper soil layer than would be measured with a narrow cavity of the same length and at the same depth.

(*c*) *Value of the method*

The analysis presented in the previous section shows in a general way why piezometers of various diameter do not lead to consistent results in the present study. Both measurements and analysis show the same trend. It thus follows that anisotropy calculations, using the piezometer method, may lead to erroneous conclusions when applied to conditions in which the assumptions implied in the theory are not approximately fulfilled.

The weakness in the method seems to lie in the use under these conditions of the tube method, which yields an apparent hydraulic conductivity value for only a small sample volume. Use of a very large sampler makes the method cumbersome; also in this way a representative value for $(k_h k_v)^{\frac{1}{2}}$ would still only be obtained for a small depth interval. The same difficulty would be encountered with the experimental method of Childs *et al.* (1957), where the tube method is also used to obtain $(k_h k_v)^{\frac{1}{2}}$.

A large variability in apparent hydraulic conductivity, as found in the present study with the tube method, was not encountered in the study on hydraulic conductivity by Talsma and Flint (1958). The reason for the relatively low variability in their study is that most of the data were obtained with the augerhole method. This method measures the hydraulic conductivity of a fairly large sample and is mainly a measure of the horizontal component of hydraulic conductivity (Maasland, 1956).

These authors (Talsma and Flint, 1958) concluded from their data that the decrease of apparent hydraulic conductivity with depth is mainly due to compression, although the possibility that this decrease may be partly due to a gradual decrease of biological activity with depth was recognized. Compression was considered to be the main factor since it is known that root activity under the present-day system of irrigation is confined to the soil above the watertable. However, the distribution of the apparently permanent channels, formed in the soil prior to irrigation, can be equally important. In the present study this is especially valid for the vertical component of hydraulic conductivity.

The piezometer and tube methods have been of importance in elucidating these factors. The augerhole method, which gives an average apparent conductivity over a relatively large sample is less suited for this purpose, but would appear to be more appropriate for routine tile drainage investigations, where an average conductance over a large part of the profile is required.

Acknowledgements

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SOIL STRUCTURE AND FABRIC

THEIR DEFINITION AND DESCRIPTION

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Summary

Definitions of structure, fabric, and texture, as used in pedology and geology, are proposed in which structure conforms to the broader concept of the soil physicist, fabric conforms to the concept as used in pedology by Kubiena (1938) and in sedimentary petrology (Pettijohn, 1949), and texture conforms to the broad concept as used in petrology (Rice, 1954). Fabric is a part of structure, and structure a part of texture. The term pedality is proposed for the study of what has been called structure in the field, and field grading for field texture. Kubiena's (1938) concepts of skeleton and plasma are defined more specifically, and the concepts of pedological features, and basic, elementary, primary, secondary, and tertiary structure introduced. Descriptive terms for structure are suggested and a descriptive system for soil materials proposed. Nomenclature of pedological features and the various levels of structure and fabric are discussed.

1. *Introduction*

THE study of soils, whether aimed at soil classification or the interpretation of soil genesis, involves the description of a great number of characteristics. Of late, the realization that soils are extremely complex materials has indicated the need for more detailed and comprehensive description. To make this mass of descriptive data understandable and manageable it is necessary to organize it into logical units which deal with the characteristics of some particular aspect of the soil material. One such aspect is its physical constitution. Although the importance of this aspect has been recognized in field pedology, soil physics, and soil mechanics, the terms used are ambiguous and the present systems of soil description are inadequate for the more recent detailed studies.

It is the object of this paper to define concepts and terms to cope with the description of the physical constitution of soil materials having regard to current concepts as used in pedology and the related science of geology.

In petrology the essential characteristics of the physical constitution of rocks have been enumerated and grouped in various ways. Although these groupings do vary they all deal with all or some of the following features of the solid particles: their crystallinity, shape, size, and arrangement. Since this approach is logical and has been proved in petrology and to a lesser extent in pedology it is proposed to apply it for developing concepts and terms for the description of the physical constitution of soil materials having due regard to their special nature. It should be emphasized at the outset that these concepts concern only the qualitative description of the physical constitution of soil materials as distinct from quantitative estimations and descriptions of complete soil profiles.

2. *Terminology and Definitions*

It is proposed to consider the current terminology as applied to the physical constitution of rocks and soil materials and so attempt to arrive at a systematic, universally applicable terminology for soil materials.

(*a*) *Fabric*

The simplest concept for describing the physical characteristics of soil materials and rock is that of fabric. In igneous petrology, fabric is defined as 'that part of texture* which depends on the shapes and arrangement of the constituents of a rock' (Rice, 1954). In sedimentary petrology, fabric is 'the orientation in space of the elements of which a rock is composed' (Pettijohn, 1949). These two petrological definitions differ only in that no mention of shape is made in the latter. Kubiena (1938) was the first to speak of soil fabric as a counterpart of rock fabric. He later (1953) used the term as 'the arrangement of the constituents, not only in the narrow sense of aggregate formation but in a general sense, referring also to the variable minor fabric of dense soil masses etc.' There is general agreement then that fabric deals primarily with *arrangement* of the constituents. However, in its application to soil materials it is considered that the definition should deal specifically with the arrangement of voids which has been considered only as a complementary result of the arrangement and packing of the solid particles. Thus:

Soil fabric is the physical constitution of a soil material as expressed by the spatial arrangement of the solid particles and associated voids.

Since soil fabric is concerned with spatial arrangement it is described in terms of the orientation and distribution patterns of the primary particles, compound particles, and voids.

(*b*) *Structure and pedality*

The petrological concepts of structure (Krumbein and Sloss, 1955; Pettijohn, 1949) which deal with regional features of sedimentary rocks or specific arrangements (the sedimentary features of Shrock (1948)) are generally unsuitable for soil materials. In pedology there are three variations of the concept of soil structure which overlap in their treatment of the physical characteristics of soil materials.

1. Baver's (1948) concept—'the arrangement of the soil particles'—considers 'the arrangement of sand, silt and clay, and of secondary particles (aggregates or structural elements) into a particular structural pattern'; size and shape of the particles are not considered. This concept is almost identical with that of fabric defined earlier.

2. Zakharov's (1927) concept—'the very fragments or clods into which the soil breaks up'—considers only the size and shape of Baver's secondary particles and ignores arrangement.

3. The concept of the U.S.D.A. Soil Survey Manual (1951)—'the aggregation of primary soil particles into compound particles, or clusters of primary particles, which are separated from adjoining aggregates by

* Texture is used here in its specific petrological sense.

surface weakness'—considers the size, shape, and arrangement of Baver's secondary particles but ignores primary particles.

These three variations encompass most of the shades of meaning implied by definitions put forward by various pedologists from time to time. Butler (1955) states that Zakharov's (1927) concept is the one applicable to the study of soils in the field. Kubiena (1953) uses structure in a similar way. Jongerius (1957) uses it in a similar way to Baver (1948) except that he considers also the arrangement of the voids. It is apparent that these variations are due to the different interests of the various workers and the sensitivity of their techniques but they may be combined logically in a single definition.

Soil structure is the physical constitution of a soil material as expressed by the size, shape, and arrangement of the solid particles and associated voids, including both the primary particles to form compound particles and the compound particles themselves. Thus fabric is the element of structure which deals with arrangement.

Soil-structure studies in the field, because of the techniques available, are concerned chiefly with the size, shape, and arrangement of compound particles to which the term pedality has been applied.

Pedality is the physical constitution of a soil material as expressed by the size, shape, and arrangement of the compound particles or peds.

(*c*) *Texture and field grading*

In igneous petrology texture is an extension of structure to include the degree of crystallization (crystallinity) while in sedimentary petrology it is synonymous with the definition of structure given earlier (Pettijohn, 1949). In pedology, texture has been used with various shades of meaning as an estimation of the percentage of clay-size particles, the complete particle-size distribution, the effects of structure, and consistence on the feel of a soil material of particular particle-size distribution, and other allied properties (Robinson, 1949; U.S.D.A. Soil Survey Manual, 1951; Leeper, 1952, &c.). Such concepts are quite incompatible with those used in petrology which come closer to normal English usage of the term.

It is realized that texture as used in pedology, although ill defined, is strongly established, but a very strong case exists for redefining the term in line with the petrological meaning and substituting another term for the present pedological concept. The following terms and definitions are suggested:

Soil texture is the physical constitution of a soil material as expressed by its structure and by the degree of crystallization (crystallinity) of the solid particles. Thus fabric is a part of structure which is a part of texture in this context.

Field grading is the assessment of the particle-size distribution by the method of moistening and manipulation of the soil material in the hand.

The relationship between the proposed pedological terms and those currently used in pedology and geology is summarized in Table 1.

TABLE I

Relationships of Proposed Concepts to Current Concepts

		Proposed Pedological Usage					*Current Pedological Usage*					*Geological Usage*						
Characteristics	*Soil components*•	*Field grading*	*Pedality*	*Fabric*	*Structure*	*Texture*	*Field texture (U.S.D.A. manual)*	*Fabric (Kubiena)*	*Structure (Zakharov)*	*Structure (Baver)*	*Structure (U.S.D.A. manual)*	*Grade*	*Packing*	*Fabric (sedimentary)*	*Fabric (igneous)*	*Structure† (sedimentary)*	*Texture (sedimentary)*	*Texture (igneous)*
Crystallinity																		
	Skeleton grains					×												×
	Peds					×												
	Pedological features					×												
	Plasma					×												×
Size																		
	Skeleton grains	×			×	×	×					×				×	×	×
	Peds		×		×	×			×		×							
	Pedological features				×	×												
	Plasma grains	×			×	×	×					×				×	×	×
	Voids				×	×												
Shape																		
	Skeleton grains				×	×												
	Peds		×		×	×			×		×							
	Pedological features				×	×												
	Plasma grains				×	×												
	Voids				×	×												
Arrangement																		
	Skeleton grains			×	×	×		×		×			×	×	×	×	×	×
	Peds		×	×	×	×		×		×	×							
	Pedological features			×	×	×		×										
	Plasma			×	×	×		×		×			×	×	×	×	×	×
	Voids			×	×	×												

• For geological usage substitute rock components, viz. solid elements and voids.
† Restricted usage e.g. oolitic structure, equivalent to sedimentary features.

3. *Application to Soil Materials*

(*a*) *The nature of soil constituents*

To apply the concepts of structure and fabric to soil materials it is necessary to consider the nature of the materials and the kinds of phenomena which may occur. In considering soil materials it must be recognized that they are composed of two broad groups of constituents with very different properties; one which is relatively stable and one which is capable of remarkable movement, concentration, and reorganization during soil formation. Each of these groups is composed of diverse constituents but it is the activity of the latter which causes many of the significant features of soil materials. Kubiena (1938) has referred to the relatively stable soil constituents as 'fabric skeleton' and to the mobile, active constituents as 'fabric plasma'. The adjective 'fabric' seems unnecessary and rather misleading since the terms really refer to the components of the soil materials. Since Kubiena has not defined these terms concisely they are defined here retaining his original concepts:

1. *Skeleton grains* of a soil material are individual grains which are relatively stable and not readily translocated, concentrated, or reorganized; it includes mineral grains and resistant siliceous and organic bodies larger than colloidal size. Complex grains are not considered as skeleton grains but as pedological features (see later). The skeleton, as such, is relatively immobile except for processes such as washing down cracks, but it is capable of weathering to form plasma.

2. *Plasma* of a soil material is that part which is capable of being, or has been moved, reorganized, and/or concentrated by the processes of soil formation. It is the mobile active part of the soil material. The plasma includes all the material, mineral or organic, of colloidal size and relatively soluble material which is not bound up in the skeleton.

It is proposed that living roots, soil fauna, and flora should not be considered as part of the soil materials as regards description of their physical constitution in terms of structure and fabric; the soil material is regarded simply as the medium for their activities although its structure may be affected by their activities. Similarly, recognizable undecomposed organic remains are not considered. These are materials with characteristics so different from the mineral constituents that they require a different method of treatment. Humified organic matter, however, can be considered in structure and fabric descriptions. Humification releases mobile organic constituents, which are part of the plasma, and resistant siliceous and organic bodies which can be included in the skeleton.

(*b*) *The organization of soil constituents*

The reorganization of constituents within soil materials due to the nature of the constituents and of the soil-forming processes, including the activity of soil fauna and plant roots, leads to the development of a series of features with specific fabrics and structures. Other features may be inherited from the parent rock or from the processes of deposition of transported parent materials. All these features are the pedological equivalents of what Shrock (1948) refers to as sedimentary features such

as cone-in-cone structure, oolitic structure, animal tracks and trails, &c. Following this nomenclature it is proposed to refer to these features, as a group, as *pedological features* which can be subdivided into various kinds.

Pedological features are recognizable units within a soil material which are distinguishable from the enclosing material for any reason such as origin, differences in concentration of some fraction of the plasma, or differences in arrangement of the constituents (fabric).

These pedological features can be divided into two broad groups on the basis of origin:

1. *In situ* pedological features which are formed in the soil profile. Of these the three chief features which have been recognized so far are:

Plasma concentrations which are concentrations of any of the fractions of plasma in various parts of the soil material, due to soil formation. Examples of these are carbonate nodules, iron-oxide nodules, clay-mineral coatings.

Plasma separations which are features characterized by a significant change in the arrangement (fabric) of the constituents, rather than a change in concentration of some fraction of the plasma. An example of this is the change in orientation of the clay-mineral fraction near the surface of slickensides.

Fossil formations which are preserved features resulting from biological activity such as burrows and root channels. These may or may not be filled with various materials.

2. Inherited pedological features which are, in fact, relicts of the soil parent rock or parent material. The three inherited pedological features recognized so far are:

Litho-relicts which are derived from the parent rock and usually recognizable by their rock structure and fabric, for example, so-called 'floaters' of parent rock.

Pedo-relicts which were formed as *in situ* pedological features in a previously existing soil material and later transported and deposited with the present parent material, for example, transported abraded nodules and concretions.

Sedimentary relicts which are formed during deposition of a transported soil parent material, for example, clay galls and clay flakes.

Besides the formation of pedological features, soil materials may become more highly organized by the development of peds. A highly aggregated soil material may have primary peds packed or bound together to form secondary peds, which in turn may form tertiary peds, and so on; in this context primary peds are the smallest recognizable natural aggregates in the soil material. The structure of such a soil material can be described systematically at several levels of organization:

(i) The size, shape, and arrangement of the constituent grains and voids within the primary peds.

(ii) The size, shape, and arrangement of primary peds and the interpedal voids to form secondary peds, and the relationships of the primary peds with materials which may occur between the peds.

(iii) Similarly, higher levels can be described in terms of the characteristics of the peds of the appropriate level, the interpedal voids,

and their relationships with each other and with materials which may occur between the peds.

The structure of interpedal material can be described separately; usually it belongs to one or other of the pedological features.

In a similar way, pedological features can exhibit levels of organization. For example, it has been observed that plasma concentrations, such as carbonate nodules, may be made up of a group of dense bodies of strongly concentrated carbonates set in a larger body of less strongly concentrated carbonates. Thus, the structure of the smaller dense concentrations can be described as well as that of the larger composite concentrations. Similar complexities have been observed in other kinds of pedological features.

The description and classification of these complex soil structures and fabrics can be approached in a logical sequence. The following definitions split the observations into usable units, any one of which can be studied separately or in relation to any other one or more.

1. *Basic structure* is the size, shape, and arrangement of simple grains (skeleton grains and plasma) and voids in primary peds, or in an unaggregated soil material within which there are no observable pedological features other than plasma separations. Complex pedological features have a basic structure for each part which shows a distinctive structure or fabric.

2. *Elementary structure* is a characteristic size, shape, and arrangement of *specific* pedological features with regard to the basic structure of the material associated with them and to specific reference features.*

Elementary structure does not necessarily deal with all the pedological features present but only those kinds which contribute to a characteristic structure. For example, strongly oriented coatings of clay minerals in root channels may occur frequently associated with a particular basic structure. This characteristic association constitutes an important elementary structure which can be described and named. Thus elementary structure is a concept of convenience. It is useful also for complex pedological features.

3. *Primary structure* is the size, shape, and arrangement of all of the pedological features present within the primary peds, or in an unaggregated soil material, with regard to the basic structure and to specific reference features. It is the complete structure of the primary peds or the unaggregated soil material.

4. *Secondary structure* is the size, shape, and arrangement of the primary peds, interpedal voids, and associated interpedal pedological features. Unaggregated soil materials do not have secondary structure or structures of higher order.

5. *Structures of higher order* deal with the size, shape, and arrangement of the peds of one order lower, and the associated interpedal voids and pedological features. Thus tertiary structure deals with the size, shape, and arrangement of secondary peds, interpedal voids and associated pedological features, quaternary structure with tertiary peds, and so on.

* Reference features are features which can be specified such as the surfaces or shapes of peds and pedological features, the walls of voids, inter-horizonal contacts, &c.

6. *Complete structure* of a soil material is the size, shape, and arrangement of all the pedological features in relation to the structure of the soil material, at all levels of organization.

The schedule of description of soil structure is set out in Table 2. This is not the only possible sequence of description and individual workers may find it convenient to rearrange the order of treatment for specific purposes.

4. *Nomenclature*

From the foregoing concepts of structure and fabric it is apparent that full descriptions will be unavoidably complex and lengthy (see Appendix). These descriptions can be abbreviated and simplified by the judicious application of names to specific, important structures and fabrics. This emphasizes the urgent necessity for a system of nomenclature. It is not intended to set out here a series of names and corresponding descriptions but rather to propose a systematic method of naming structures and fabrics at various levels of organization. Since the same principles apply to naming both structure and fabric, structure only is considered here for conciseness.

At the lowest levels of organization basic structures and pedological features are relatively simple and limited in number. Once these have been characterized and named the structures at higher levels, which will be more numerous and complex, can be described in terms of specific combinations of these features. Thus, elementary structure is described in terms of basic structure and one or more specific pedological features and primary structure in terms of basic structure and all included pedological features. Since structures at still higher levels are classified on the characteristics and arrangement of the peds, rather than in terms of basic structures and pedological features, they can be named independently. It is essential, therefore, that standard common basic structures, pedological features and structures at the secondary and higher levels be classified and named.

Pedological features can be classified and named on characteristics of shape, sharpness of separation, kind of material (which is not really a part of the structure description), orientation and distribution patterns, and internal structure. A few of these features, such as 'amygdali' (McMillan and Mitchell, 1953) have been described and subdivided according to their structure and fabric. Others such as 'crystal tubes' have been described by Kubiena (1938).

Basic structures are named solely on the characters of the elements of structure within the material. Kubiena's (1938) elementary fabrics apparently are akin to basic fabrics.

Elementary and primary structures can be described in terms of basic structure and associated pedological features. Characteristic ones should be named.

Secondary structures and structures at higher levels can be classified and named on the characters of the elements of structure considering the peds as skeleton units equivalent to skeleton grains in structures at lower levels. Kubiena (1938) has applied names to 'fabric members of higher

TABLE 2

Description of Structure

Structure level	*Material*	*Components*	*Characteristics*		
Pedological features	Individual pedological features*	Skeleton grains Plasma grains Voids	Size	Absolute and relative	
Basic structure (including plasma separations)	Material within primary peds but excluding pedological features other than plasma separations	Skeleton grains Plasma grains Voids	Shape	Shape and roundness classes; absolute and relative	
Elementary structure	Material within primary peds including that with basic structure and specific characteristic pedological features	Skeleton grains Plasma grains Voids Specific pedological features as units	Arrangement	Orientation pattern	1. Orientation of individuals with each other. 2. Referred orientation—with regard to a reference. 3. Orientation between groups of individuals.
Primary structure	All material within primary peds (material with basic structure and all pedological features)	Skeleton grains Plasma grains Voids Pedological features as units		Distribution pattern	1. Distribution of individuals with regard to each other. 2. Referred distribution—with regard to a reference. 3. Distribution between groups of individuals. 4. Sharpness of boundary.
Secondary structure	Primary peds as units and interpedal pedological features	Primary peds Interpedal voids Interpedal pedological features			
Tertiary structure	Secondary peds as units and pedological features between secondary peds	Secondary peds Interpedal voids Interpedal pedological features			

* Pedological features may have levels of organization requiring description in terms of several basic structures and their relations to each other.

order' but these do not seem to fulfil consistently the requirements for application to structures or fabrics of higher order proposed here.

Finally, *complete structures* can be classified and named but these will be very numerous and very complex. Kubiena's (1956) fabric names for whole soil materials do not seem to be suitable for this concept of complete structures or fabrics; they appear to be too generalized to succeed for complete soil materials.

In the actual naming of these structures at the various levels of organization there are two important points to consider:

1. Since structure and fabric analyses are not considered in any of the classification systems in use at the present time, the names of any of the soil groups at any level in any of these classification systems should not be used. An additional reason for this is that structure and fabric can be described only for a soil material and not a profile, since they may vary down a soil profile. Names should refer specifically to the characteristics observed and described; they should be coined, or selected from geographical names, and given specific meaning.

2. It is possible that fabrics at different levels may be identical. For example, a well-aggregated soil material may have its primary peds organized to form secondary peds in the same manner as the secondary peds are organized to form tertiary peds and so on. Thus, the secondary, tertiary, and higher level fabrics may go under the same name.

5. *Discussion*

It is considered that the proposed definitions of structure and fabric given above are justified by the fact that they include all the concepts which have been used in pedology and fulfil the needs of workers in all branches of pedology. In addition, the concepts have a systematic relationship to each other: structure embraces all the characteristics of the physical constitution of the soil material except crystallinity, while fabric and pedality are specific parts of structure. Field grading is considered a more appropriate term than 'field texture' for particle-size distribution assessments in the field; 'texture' should be reserved for the complete physical constitution, i.e. structure plus crystallinity.

One of the major difficulties in dealing with the description of soil structure and fabric, is the scale at which the observations are made. It cannot be emphasized too strongly that the definitions of fabric and structure place no limitations on the scale of development of phenomena so that observations at all possible magnifications must be considered. In this paper, the descriptive terms have been defined to cover as wide a range of scales as possible, but it is obvious that some of the characteristics can be observed only under the petrological microscope, not only because of the scale of development but also because this is the only possible technique for observing them. Again, no characteristics beyond the resolving power of the petrological microscope have been used. This is a limitation which may be partly overcome by electron microscopic studies, e.g. it is known that up to 60 per cent. of the voids in a specific soil material may be less than 1 μ in diameter (Katchinski, 1956); such voids are not observable under the microscope. As the magnifica-

tion at which observations are made is increased it becomes possible to describe the detail of arrangement (fabric) so that descriptions of the same material may vary considerably according to the magnification used. This difficulty has been met in the schedule for description of structure and fabric by allowing for descriptions at all levels of organization; the proposed system of naming also allows for names to be attached to fabrics and structures at all levels.

Fabric and structure, as such, do not take account of the frequency of occurrence of the constituents of a soil material; they are not measurable quantities. However, they do include descriptions of size and shape of the constituents together with an estimate of the variability of these characteristics. Such descriptions indicate the probability of sorting, when applied to skeleton grains, but not absolute frequency of occurrence. Thus, the descriptions are chiefly qualitative. Quantitative studies of particle-size distribution, void-size distribution, &c., must be made separately by the accepted techniques if they are to be accurate and if the results are to be analysed in terms of populations and distributions. As Low (1954) points out, such measurements are not measurements of structure.

Again, fabric and structure are not actually concerned with the mineralogical or chemical identification of the constituents of the soil material, or the colour of the constituents. However, in making observations, especially at the microscopic stage, variations in colour may reflect variations in mineralogy which in turn reflect variations in concentration and separation of the plasma and perhaps in orientation and distribution of the plasma grains (fabric). Thus, these characteristics are used in classifying and naming pedological features, as a matter of convenience, although such features can be described without reference to such characteristics.

It should also be noted that the descriptive system and schedule are directly applicable to texture as defined earlier. If crystallinity is included, the word 'texture' can be read for 'structure'. Thus, all of the terms basic texture, elementary texture, primary texture, secondary texture, &c., are applicable.

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APPENDIX

DESCRIPTIVE SYSTEM

MANY of the terms used in the description of rock texture are directly applicable to soil structure but some additions and modifications are necessary. The characteristics requiring description are summarized in Table 1. The proposed terms are based mainly on megascopic and microscopic examination.

1. *Absolute size* — (*a*) *Size and Shape*

Extremely fine	$< 0{\cdot}005$ mm.
Very fine	0·02–0·005 mm.
Fine	0·1–0·02 mm.
Medium	0·5–0·1 mm.
Coarse	2·0–0·5 mm.
Very coarse	10–2 mm.
Extremely coarse	$>$ 10 mm.—specify actual size

2. *Absolute shape*

(i) *Shape classes*: after Zingg (1935) with the following additions and modifications.

Prolate (rods)	$b/a < 2/3$ but $> 1/10$; $c/b > 2/3$
Acicular (needles or channels)	$b/a < 1/10$; $c/b > 1/10$
Planar (planes)	$b/a > 1/10$; $c/b < 1/10$
Other shapes.	

(ii) *Roundness classes*: after Pettijohn (1949).

3. *Relative size and shape*

Very even:	a strong peak in the frequency distribution curve.
Even:	a distinct peak in the frequency distribution curve.
Uneven:	a slight peak in the frequency distribution curve.
Very uneven:	irregular distribution.

(*b*) *Arrangement*

1. *Orientation pattern*

(i) *Orientation of individuals with each other*

Skeleton grains, peds, pedological features, and voids

Strongly oriented:	more than 60 per cent. of the individuals have their principal axes within 30 degrees of each other.
Moderately oriented:	40–60 per cent. have their principal axes within 30 degrees of each other.
Weakly oriented:	20–40 per cent. have their principal axes within 30 degrees of each other.
Unoriented:	There is no preferred orientation.

Plasma. If individual plasma grains are large enough the terms used for skeleton grains are applicable. However, they are usually ultramicroscopic, and only aggregates (plasma aggregates) of individual grains are large enough to be recognized. Thus the orientation of clay-size particles can be stated only for anisotropic materials where it is reflected in the extinction phenomena in thin section at various magnifications. The most useful magnifications have been found to be approximately 30×, 80×, 200×, 800×, 1200×. The descriptions are made at each of these magnifications and the increasing observable degree of orientation with increasing magnification is noted as a comparative measure of orientation.

Strongly oriented: at the magnification used the plasma aggregates are continuously birefringent in thin section, that is, under crossed nicols dark extinction lines run across the aggregates or they extinguish as a unit.

Moderately oriented: at the magnification used the plasma aggregates have rather indistinct boundaries and have an incomplete mottled or fuzzy extinction reminiscent of the extinction of some micas.

Weakly oriented: at the magnification used the plasma aggregates are anistropic but too small to observe in detail so that the mass has a flecked appearance.

Unoriented: at the magnification used the plasma appears isotropic because of the low degree of orientation.

Indeterminate: the plasma is isotropic because of its crystallographic nature or opacity.

Crystallized: the plasma occurs as crystals large enough to be described in the terms used for skeleton grains.

Besides the orientation of individual plasma grains with each other, the plasma aggregates, especially if they are not equidimensional, may have various patterns of orientation observable at various magnifications. The degree of development of these arrangements is recorded at each magnification as a further measure of orientation.

Continuous orientation. This applies especially to pedological features which consist entirely of a single unit of strongly oriented plasma.

Striated orientation. The plasma aggregates have a lineal arrangement:

Strongly striated:	more than 60 per cent. of the material has a lineal arrangement.
Moderately striated:	20–60 per cent. of the material has a lineal arrangement.
Weakly striated:	less than 20 per cent. of the material has a lineal arrangement.

Flecked orientation. The plasma aggregates are arranged randomly.

(ii) *Referred orientation.* If a group of individuals have a preferred orientation then this can be referred to prominent directions or surfaces within the soil material, such as ped faces, systems of planes, &c., or to the ground surface:

Parallel orientation:	the principal axes of the individuals are parallel to the reference.
Normal orientation:	the principal axes are normal to the reference.

Transverse orientation: the principal axes are at an angle to the reference; this angle should be stated.
Unrelated orientation: there is no constant relationship with the reference.

(iii) *Orientation between groups of individuals.* The orientation of one group of oriented individuals can be stated with regard to other groups. The terms parallel, normal, transverse, and unrelated are applicable.

2. *Distribution pattern.* Individual plasma grains are usually too small, unless crystallized, to describe their distribution patterns. However, where pedological features have been formed these can be treated as entities whose size and shape can be described according to the terms already listed, and whose distribution pattern can be described. Pedological features also require a description of the sharpness of their boundaries which is an expression of the distribution of the plasma fractions within the pedological features.

(i) *Sharpness of boundary of pedological features.*

Very diffuse: no boundary is observable.
Diffuse: gradual transition over a distance greater than one-quarter of the shortest dimension of the feature.
Rather diffuse: gradual transition over a distance between one-quarter and one-tenth of the shortest dimension of the feature.
Rather sharp: gradual transition over a distance of less than one-tenth of the shortest dimension of the feature.
Sharp: the boundary is quite sharp.

(ii) *Relationship of plasma grains and skeleton grains in the basic fabric.*

The terms used follow those used by Kubiena (1938) as far as possible.

Porphyritic: the plasma occurs as a dense matrix in which the skeleton grains are set after the manner of phenocrysts in a porphyritic rock.
Agglomeratic: the plasma occurs as loose or incomplete fillings in the intergranular spaces between the skeleton grains.
Intertextic: the plasma occurs as intergranular braces linking the skeleton grains.
Granular: there is no plasma, or all the plasma occurs as pedological features.

Undoubtedly additional terms will be necessary to describe other specific arrangements as more data are collected.

(iii) *Distribution of individuals with regard to each other* (skeleton grains, voids, peds, pedological features).

Regular: distributed evenly throughout the soil material.
Clustered: concentrated in clusters or groups.
Banded: concentrated in bands or layers.
Other patterns: other possible patterns are radial, concentric, &c.

(iv) *Referred distribution.* The distribution of individuals or groups can be referred to prominent directions or surfaces within the soil material or to the ground surfaces. For elongated patterns the terms parallel, normal, transverse, and unrelated, as used for the orientation pattern can be used to indicate elongation in regard to a specific reference. In addition, the following terms are useful applied especially to pedological features.

Cutanic: associated with natural surfaces.
Sub-cutanic: the pattern is elongated parallel to adjoining natural surfaces.
Non-cutanic: unrelated to natural surfaces.

(v) *Distribution between groups of individuals.* Within the one soil material, certain groups of individuals (shape classes, oriented groups, &c., of voids, skeleton grains, peds or pedological features) may have a particular distribution pattern with regard to other groups. Such patterns, if characteristic, should be described and given a descriptive name.

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